

TP  
290  
T856

UC-NRLF



\$B 32 056









**TNT**  
**TRINITROTOLUENES**  
**AND**  
**MONO- AND DINITROTOLUENES**

**THEIR MANUFACTURE  
AND PROPERTIES**

**BY**

**G. CARLTON SMITH, B.S.**

*Instructor in General Chemistry, School of Applied Science,  
Carnegie Institute of Technology, Pittsburgh, Pa.*



**OHIO STATE  
UNIVERSITY**

**NEW YORK**  
**D. VAN NOSTRAND COMPANY**  
**25 PARK PLACE**  
**1918**

Б. Г.

Б. Г. (1911-1912)

Б. Г. (1911-1912)

Б. Г. (1911-1912)

Б. Г. (1911-1912)

Б. Г. (1911-1912)

Б. Г. (1911-1912)

Б. Г. (1911-1912)

Б. Г. (1911-1912)

Б. Г. (1911-1912)

**Reproduced by  
DUOPAGE PROCESS  
in the  
U.S. of America**

**Micro Photo Division  
Bell & Howell Company  
Cleveland 12, Ohio**

TP 250  
T8 56

Copyright, 1918, by  
D. VAN NOSTRAND COMPANY

Ref. # 382069

STATE OHIO

YTB33V8U

PRINTED BY  
BRADFORTH & CO.  
BOOK MANUFACTURERS  
BROOKLYN, N. Y.



TP290  
T856

TO

*My Mother*

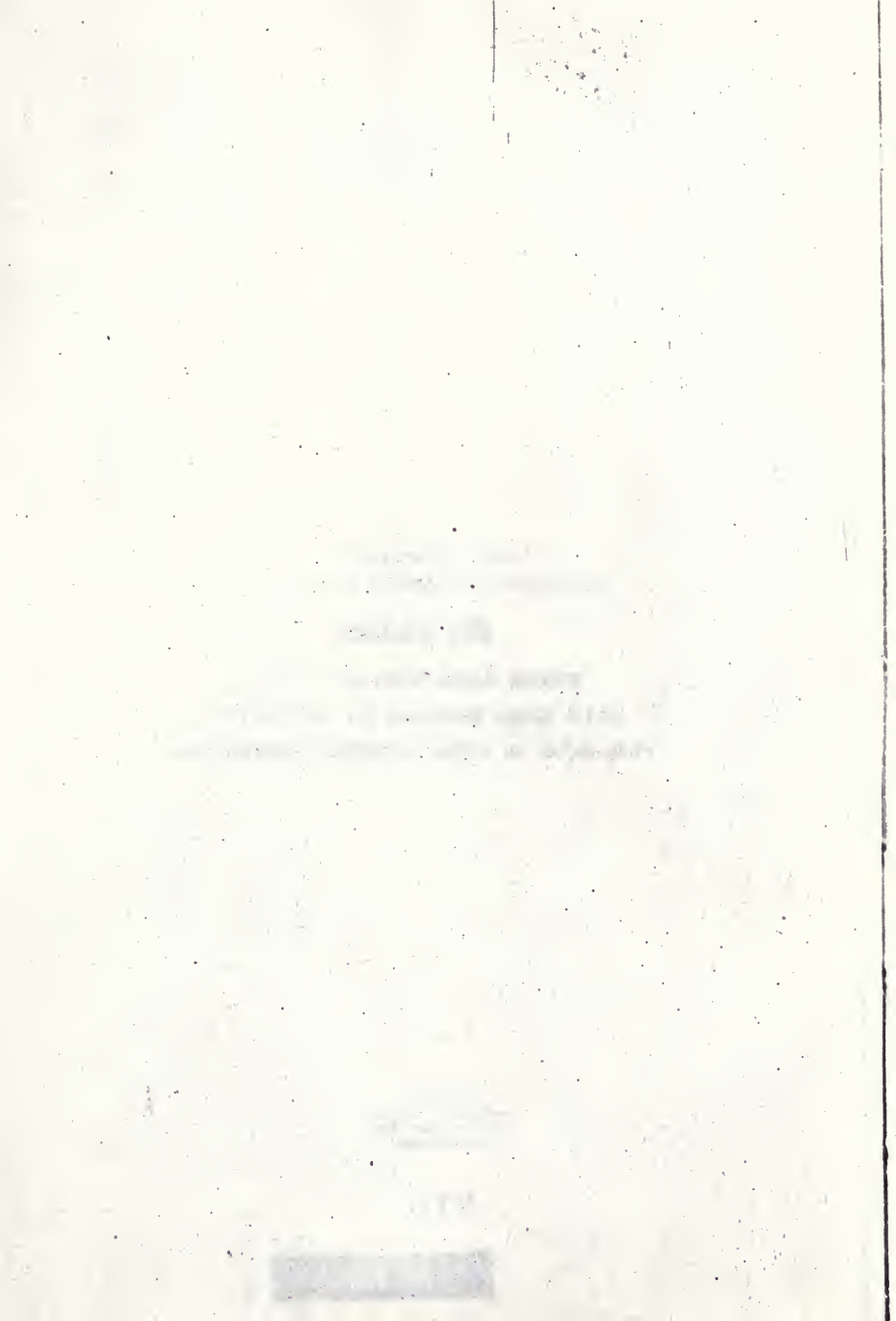
WHOSE SACRIFICES AND LOVE

HAVE MADE POSSIBLE MY EDUCATION

THIS BOOK IS AFFECTIONATELY DEDICATED

813

199135



## ACKNOWLEDGMENT

---

THE writer wishes to thank all those who have so kindly aided him in the preparation of this book.

He is especially grateful for the valued comments and criticisms offered by the members of the Staff of the Department of Chemical Engineering, Carnegie Institute of Technology; for the facts which form the basis of Chapter X, by Dr. Samuel Haythorn of the Singer Memorial Laboratory, Allegheny General Hospital; and for data on TNT manufacture by Mr. Robert M. Crawford of the Grasselli Powder Co.

The Chemical and Industrial Journals have been consulted freely, and much valuable material has been extracted therefrom.

Department of Chemical Engineering,  
Carnegie Institute of Technology,  
Pittsburgh, PA., May, 1918.





# TABLE OF CONTENTS

---

CHAPTER I	
INTRODUCTION.....	PAGE 1
CHAPTER II	
HISTORICAL.....	6
CHAPTER III	
THE THEORY OF THE NITRATION OF TOLUENE.....	20
CHAPTER IV	
THE MANUFACTURE OF TNT.....	29
CHAPTER V	
THE PURIFICATION OF TNT.....	52
CHAPTER VI	
INSPECTION AND TESTING OF TNT.....	61
CHAPTER VII	
PROPERTIES OF THE TRINITROTOLUENES.....	77
CHAPTER VIII	
PROPERTIES OF THE MONO- AND DINITROTOLUENES.....	95
CHAPTER IX	
ACCIDENTS IN TNT PLANTS.....	106
CHAPTER X	
TNT DISEASES.....	112



# TRINITROTOLUENE

---

## CHAPTER I

### INTRODUCTION

THE almost universal adoption of trinitrotoluene as the most efficient explosive in modern warfare; the development and refinement of its manufacture, and the interesting chemistry of its compounds, as well as those of the lower nitro-derivatives of toluene has prompted quite extensive research as to their composition, structure, manufacture, properties and uses. The fact that the results of these researches have been varied; often quite contradictory; somewhat disconnected and expressed with some confusion of terms would seem to warrant the publication of this little volume in which an attempt is made to gather together and correlate all accessible information on the subject, both theoretical and practical.

Since the chemical name "trinitrotoluene" is rather mysterious to the non-scientific mind, and since it is also much too lengthy for general use in this age of efficiency, concentration and hustle, there have been coined many abbreviations and substitutions of the word. In general these terms are local only, but, by

use in specifications, etc., they have spread beyond the territory in which they originated. Little wonder is caused, therefore, that the uninitiated should confuse the several names now in vogue for trinitrotoluene, and that he should think "TNT" to be one substance, "trotyl" to be another, and so on. The entire list of contractions and designations is much too lengthy to give in its entirety, but the more familiar ones are these:

"TNT"; the American contraction, and the one usually used for trinitrotoluene in this country.

"Trotyl"; this term is of English origin, and is used almost exclusively in English specifications and literature.

"Tolite"; the French abbreviation.

"Trilite"; Spanish.

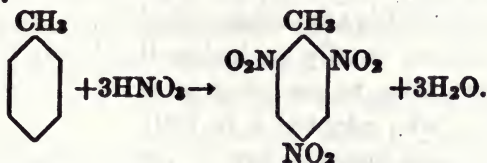
"Fullpulver-O2" or simply "Fp-O2" is used by the Germans to denote trinitrotoluene. This is, of course, neither a contraction nor an abbreviation of the name itself, but denotes merely a certain explosive in accordance with the German system of classification.

Some other terms are "Trinol," "tritol," "tritolo" and "coal tar salt," this last being the newest designation for trinitrotoluene. By comparing the above terms with the full word, the relation of most of them is easily seen.

Trinitrotoluene is just what its name implies—a triple nitrated toluene. Toluene, itself, is a liquid prepared usually from coal tar, by distillation. This is the main source of this substance in North America, although it is prepared in smaller amounts from artificial gas, the cracking of crude petroleum, etc.



By treating toluene with nitric acid, three nitro-groups attach themselves to the molecule in this manner:



This particular trinitrotoluene is one of the six isomeric compounds of that name, and is the one formed by the commercial nitration of toluene. Chemically it is the  $\alpha$ , 1-2-4-6, or "symmetrical" trinitrotoluene.

Trinitrotoluene belongs to the shattering class of explosives known as the "brisants." The members of this class possess great force, and upon exploding, shatter the containing shell into small pieces, thus doing more damage per shell.

The other well-known member of the brisant class of explosives is picric acid, or trinitrophenol. Previous to the use of trinitrotoluene, picric acid was used largely as the explosive charge in shells. There are several disadvantages in picric acid, however, which trinitrotoluene does not have. Picric acid forms salts (picrates) with a great number of the metals. These picrates are very unstable, and are quite sensitive to shock, thus giving rise to premature explosions which often result fatally. Trinitrotoluene is very inactive toward the greater number of the metals. Furthermore, picric acid has a high melting-point ( $122.5^\circ$ ) while the melting-point of trinitrotoluene is low enough ( $80.6^\circ$ ) that it may be poured into the shell in the molten state without danger from fire.

On the other hand, trinitrotoluene is not quite as powerful as picric acid, but its insensibility to shock, together with the advantages cited above, have resulted in its almost totally replacing the latter in warfare. The first nation to use trinitrotoluene in shells was the Germans, who adopted it in 1904.

The great insensibility of trinitrotoluene as compared to that of picric acid, is shown in the following table of minimum charges necessary for the detonation of both explosives:

Detonator.	TNT.	Picric Acid.
	Gram.	Gram.
Mercury fulminate.....	.36	.32
Cadmium fulminate.....	.11	.05
Silver fulminate.....	.095	.05
Mercurous azide.....	.145	.075
Lead azide.....	.09	.025
Silver azide.....	.07	.025
Cadmium azide.....	.04	.02

Aside from its use individually as an explosive, trinitrotoluene is often mixed with other ingredients. The most important of these blends, together with their analyses, are:

"Thunderite"; TNT, 4 per cent; ammonium nitrate, 92 per cent; flour, 4 per cent.

"Permonite"; TNT, 10 per cent; ammonium nitrate, 42.5 per cent; potassium chlorate, 32.5 per cent; starch, 12 per cent; wood meal, 3 per cent.

"Aluminium explosive"; TNT, 31 per cent; ammonium nitrate, 44.9 per cent; aluminium wool, 24.1 per cent.

"Plasteryl"; TNT, 99.5 per cent; resin, 0.5 per cent.

"Macarite"; TNT, 30 per cent; lead nitrate, 70 per cent.

"Donarite"; TNT, 12 per cent; col.cot. 0.2 per cent; ammonium nitrate, 80 per cent; flour, 4 per cent; nitroglycerine, 3.8 per cent.

Dinitrotoluene is also used in conjunction with other materials as an explosive. One such mixture is "Cheddite-O2." The analysis of the mixture is:

DNT, 15 per cent; potassium chlorate, 79 per cent; mononitronaphthalene, 1 per cent; castor oil, 5 per cent.

One further mixture deserves mention because of the use of DNT and TNT in the mixture. This explosive is called "triplastite." The analysis is:

Mixture of DNT and TNT, 70 per cent; col.cot., 1.2 per cent; lead nitrate, 28.8 per cent.



## CHAPTER II

### HISTORICAL

SOME doubt exists as to whom the honor of the discovery of toluene is due. Dr. W. Wilson in an article dated 1850, (1) gives the credit of the discovery to Deville, a French chemist, who obtained from balsam of tolu a compound to which he ascribed the name "benzoen." From the above article, Deville evidently did not analyze the "benzoen" but arbitrarily assigned to it the formula  $C_{14}H_{16}$ .

Beilstein and Kuhlberg, in their "Eleventh Treatise on Isomers of the Toluene Series," (2) give the honor to Pelletier and Walters, also French chemists, who obtained an oil from the distillation of pine resin, and from which oil they separated a liquid which they called "retinaphtha." Their description of this liquid is this: "It is a very clear liquid, . . . boiling at  $108^{\circ}$  C., and it is not completely solidified at  $-20^{\circ}$ . The results of three analyses indicate the formula  $C_7H_8$ ." (This is just half the molecular formula given by Deville to his substance.) "One could also give the formula  $C_{14}H_{16}$ , but there is no definite ground for such a statement. In fact, the vapor density is 3.23—the vapor density corresponding to the formula  $C_7H_8$  would be 3.226."

From this statement it would seem that Pelletier and Walters were already aware that a substance of the



formula (supposedly)  $C_{14}H_{10}$  had been isolated, and that, by determining the vapor density, they had proved it to be just half this molecular weight, or  $C_7H_5$ . On the other hand, there is no reason why—if they did know of the previous discovery of this same substance—they should give it a new name. The dates on which the above-mentioned men published their article seems to point to Pelletier and Walters as the discoverers—their work was completed about 1838, while Deville's work was published somewhere about 1841. Of course, there is the possibility that Deville completed his work some years before his results were published.

In 1843, Berzelius technically accorded the discovery of toluene to Deville by suggesting the name "toluol" or "toluene" for the compound, (3) the name being derived from "oil of tolu."

Some of the scientists of that period (probably friends of Pelletier and Walters), did not approve of Berzelius' choice of name for this substance, and two of these, Muspratt and Hoffman, in a research paper dated 1845, take occasion to remark: (4) "Berzelius has proposed for this compound the name 'toluol' or 'toluene,' names which are not very well chosen, but which we shall retain in the following discussion."

The "retinaptha" of Pelletier and Walters and the "benzoen" of Deville were proved to be the same substance by the preparation of the nitro-derivatives, and by comparing the constants of those, and possibly the acid nitro-derivatives and corresponding toluidins.

Glenard and Boudalt, at about the same time, probably later than both Deville's and Pelletier and Wal-

ter's work, isolated toluene from "Dragon's blood." (5) No further reference, and consequently no identification of this substance, could be found. Glenard and Boudalt gave the name "dracyl" to the substance they isolated. Following the methods of their predecessors they proved the identity of dracyl and toluene.

Still another man, Cahours, during the years 1847-48 isolated a substance from crude wood alcohol by treating the alcohol with sulphuric acid. He called this substance "toluen," which is so near "toluene" that naturally it would be supposed to be the same. Cahours demonstrated, however, that the formula of "toluen" was  $C_{14}H_8$ , which gives rise to a doubt as to whether his product was really identical with toluene. An abstract, dated 1849, reads thus: (6) "Cahours has separated from crude wood alcohol different oily hydrocarbons, some already known; some new. Toluene  $C_{14}H_8$  is identical with the toluene of Deville. It distills between 108 and 112° C. Cahours found the vapor density to be 3.27. Through treatment with nitric acid he obtained mono- and dinitrotoluene, and from these, by reduction with ammonium sulphide, the corresponding toluidin and nitrotoluidin."

It is rather difficult to understand why Cahours insisted on the formula  $C_{14}H_8$  after having determined a vapor density of 3.27, which so closely checked Pelletier and Walter's determination.

About 1850, Mansfield, an English chemist, isolated toluene from coal tar. (7) This discovery of Mansfield's practically ends the historical interest in toluene, since it has come to be the principal source of this substance. One further method of obtaining

toluene will be cited, however, because of its scientific interest. In 1846, two German chemists, Tollens and Fittig, prepared toluene synthetically from methyl iodide and brombenzene. (8) This method was a modification of Wurz' synthesis of the aliphatic hydrocarbons, and it is interesting because the primary product of the now commercially valuable "Fittig's synthesis" was toluene, the basis of the greatest explosive of modern times.

The earliest reference to be found concerning the purification of coal tar toluene is contained in Wilson's paper, (9) wherein he states: "The best method of obtaining pure toluene consists in collecting the part which passes over between 100 and 120° C. and treating this with one-half its weight of concentrated sulphuric acid. I have not determined which substances are removed in this process; the fact remains, however, that a constant boiling-point is obtained more easily through the use of sulphuric acid than without. The boiling-point of pure toluene was found to be 110° C. . . . Under all conditions a series of protracted distillations is necessary to obtain this object."

As is seen from this statement, Wilson followed the same method of procedure as is followed to-day in order to effect the removal of the olefines from the crude toluene. Modern plants, equipped with the latest type of fractionating stills, with their complicated columns, refluxes and fractional condensers are fortunately not put to the same trouble in the purification of toluene as was Wilson.

The history of the discovery and preparation of mononitrotoluene runs parallel with that of toluene, since it was by the preparation of the former that tol-



uene was identified by the several chemists. Deville prepared the mononitrotoluene and also the sulphonate of toluene. The nitro-compound he called "protonitrobenzoen," and describes it in this manner: "It tastes like bitter almonds; smells suffocating at first then penetrating. Its specific gravity is 1.18 at 16°. It boils at 225°." The same chemist found the vapor density to be 4.95. The vapor density as calculated by him would be 7.87, basing the calculation on his formula of  $C_{14}H_{16}$  for toluene. (10)

Berzelius, in a research paper published in 1843, gives in detail the preparation of nitrotoluene. (11) The results of a series of researches to prove its constitution are mentioned also. Berzelius was misled by his results, as was Deville. His final conclusion states, "Nitrotoluene can be considered as a nitride of toluid oxide,  $C_{14}H_{14}O = N$ ." The chemical properties of nitrotoluene were studied at length by Berzelius, but he evidently arrived at no definite conclusion regarding these properties.

Dr. Wilson, in the same article to which reference is made above, makes this statement concerning nitrotoluene: "The changing of toluene to nitrotoluene is carried out without difficulty in the usual manner. The boiling-point of nitrotoluene lies between 220 and 225° C. This body boils without decomposition." The last statement of Dr. Wilson, concerning the ability of nitrotoluene to be distilled without decomposition, confirmed experiments carried out by Glenard and Boudalt. This question was a much mooted one at this time, since other chemists had proved to their entire satisfaction that nitrotoluene could not be distilled without undergoing decomposition. Comment-

ing on this question, Beilstein and Kuhlberg (12) explain the decomposition of nitrotoluene as being due to the probable content of higher nitro-derivatives of toluene. This we now know to be the truth, and the firms who are purifying their nitrotoluene by distillation are very careful to remove all the higher nitro-compounds before attempting the distillation.

About this time, another chemist entered the field of the nitro-compounds. This man was Jaworsky. He started out his work by preparing nitrotoluene, which he claimed to be a solid, and not a liquid as Deville, Wilson, and others had thought it to be. (13) Jaworsky represents about the best type of pure industrial chemist to be found in this period of time. His work on nitrotoluene had a great effect on the industries; so much so, that at the Paris Exposition of 1867 there was exhibited a great quantity of beautifully crystallized nitrotoluene. Whether this consisted of the pure solid isomer of nitrotoluene or whether it was a mixture of one or more nitrotoluenes and dinitrotoluenes, is not known. Jaworsky was also the first to produce toluidin—the homologue of aniline—by the reduction of nitrotoluene with tin and hydrochloric acid. The immediate industrial result of Jaworsky's work was that the use of nitrotoluene as a dyestuff base was firmly established.

Kekule, the great chemist whose "benzene ring" theory is now the basic law of the chemistry of the aromatic compounds, worked exhaustively with nitrotoluene, and did much to clear the cloud caused by Jaworsky's contradiction of Deville's work. Kekule's work showed—to quote his words—"At least it is quite probable that the substance hitherto regarded as nitro-



toluene is nothing else than a mixture of nitrotoluene and nitrobenzene."

Summarizing the work of these earlier investigators of the nitrotoluenes, there is one fact that stands out very clearly throughout all their work—they had no thought of the possible isomerism of nitrotoluene. The results obtained by all the various work done by these chemists was finally interpreted by Kekule as meaning that nitrotoluene was a solid, and that the liquid obtained by Deville and others was a liquid only because of the admixture of nitrobenzene.

This cloud began to disappear with the work of Rosenstill, who was the first to suggest the possibility of the existence of nitrotoluene in different forms. His work was later supplemented by Beilstein and Kuhlberg, who found in Rosenstill's work the hint that led to their isolation of the three isomeric nitrotoluenes, and the classification and naming of these compounds. The results of Beilstein and Kuhlberg's work was published in 1879, when, for the first time, the true constitutions of the nitrotoluenes was established.

It is very peculiar, indeed, that most of the brilliant earlier chemists, whose work did so much to lay the foundation of the present wonderful science, wound up their work with a probable error. The word "probable" is used intentionally, because in that formative period of the chemistry of the aromatics, with the constantly arising theories and hypotheses, there may appear errors which are in reality not such, but which were facts when viewed in the light of the then accepted laws. Future discoveries have changed many of these early ideas, and possibly it may be better

to state that they were led astray by statements and hypotheses which later proved to be without foundation. The particular point to which I refer is the nomenclature used by Beilstein and Kuhlberg for the nitrotoluenes. This may appear a small matter, but when reference is made to the publications of these men, and when these references are viewed in the light of present day accepted facts, their nomenclature is confusing. More so, because they made use of the terms "ortho," "meta," and "para," which are the same as are used to-day. The meta and ortho isomeric nitrotoluenes appear to be just reversed from those isomers now regarded as meta and ortho. This view was not due to Beilstein and Kuhlberg alone, for at least one other scientist, V. von Richter, was of the same mind. Von Richter states thus: (14) "Trinitrotoluene from *meta* mononitrotoluene crystallizes in yellow needles which melt at 82°." Now, the meta mononitrotoluene, according to modern orientation, will have the nitro-group in position three. (Throughout this book the methyl group in toluene will be considered as occupying position *one*.) The trinitrotoluene that has a melting-point of 82° (probably slightly incorrect), is the symmetrical trinitrotoluene, with the nitro-groups in positions 2-4-6. It would therefore be impossible for this symmetrical trinitrotoluene to result from what von Richter and Beilstein call meta nitrotoluene, unless one nitro-group actually shifts its position in the molecule which, as is known, is impossible with the conditions existing as they do in the process of nitration.

Returning, now, to Beilstein and Kuhlberg, and their "Eleventh Treatise," there is found a detailed summary of the constants of three nitrotoluenes:

	Melting-point.	Boiling-point.
Ortho.....	16	230-231
Meta.....	.....	222-223
Para.....	54	235-236

These same constants of the nitrotoluenes named as we have them to-day, are different:

	Melting-point.	Boiling-point.
Ortho.....	-10.5	218-220
Meta.....	16	230
Para.....	54	234

By comparing the above summaries, it is seen that the ortho compound of the earlier chemists is identical with the present meta nitrotoluene, and vice versa. That the early view was incorrect may be further proved by investigating the properties of the meta compounds. In all reactions the meta compounds react differently from the ortho and para compounds. For instance, in the nitration of toluene, the ortho and para nitrotoluenes are formed in large amounts, and the meta in small amounts. Further, when the mononitrotoluenes are nitrated to dinitrotoluene, the ortho and para mononitrotoluenes are very easily nitrated further, and the meta difficultly so. In other words, the ortho and para compounds form one part of the class, while the meta stands alone as the other part. With the early nomenclature, the meta and para would be placed together, while the ortho would stand alone. If, now, this view of the matter is accepted, Von Richter's statement becomes entirely correct.



After Beilstein and Kuhlberg completed their work on the nitrotoluenes, they set about investigating toluene to discover whether or not this substance existed in isomeric forms, thinking thereby to explain the isomerism of the toluene derivatives. Their experiments are interesting in the extreme, but are too lengthy to discuss in this book. Suffice it to say that the results of their research proved conclusively that toluene existed in but one form.

In considering the discovery of dinitrotoluene, we must again give the credit to Deville. His original paper on the general subject of toluene and its nitration derivatives contains the statement that he prepared the dinitro-compound, which he called "binitrobenzoen," in direct accordance with the scheme of nomenclature he adopted. Deville gives the melting-point of his preparation as  $71^{\circ}$ . Therefore it is inferred that his "binitrobenzoen" was 1-2-4 dinitrotoluene. (15)

Cr. hours also prepared a dinitrotoluene, but unfortunately he did not leave any data as to which of the isomers he obtained.

Beilstein and Kuhlberg prepared two dinitrotoluenes, but give the melting-point of but one of the two. This was the same as that of Deville. The work of Beilstein and Kuhlberg seems to have been mostly on the mononitro-compounds of toluene, and the acidic and basic compounds of mononitrotoluene.

Dr. O. Cunerth, in a paper dated 1874, (16) gives probably the most comprehensive summary of the history and discovery of the dinitrotoluenes to be found. His paper begins with this statement: "It is known that in the nitration of toluene, two modifications are

obtained; the ortho and para." This statement is further proof that Beilstein was mistaken in his nomenclature.

The second dinitrotoluene was discovered by Rosenstill, but he was not sure whether it was the 1-2-3, the 1-2-5, or the 1-2-6 compound. Dr. Cunerth, after much work, identified this dinitrotoluene as the 1-2-6 modification.

The 1-3-4 dinitrotoluene was discovered by Beilstein, who did this work independently of Kuhlberg in 1873. It was then that Beilstein gave the names to the three known dinitrotoluenes. The 1-2-4 modification he called the  $\alpha$ ; the 1-2-6, the  $\beta$ ; and the 1-3-4, the  $\gamma$ . This nomenclature is not strictly adhered to, by modern chemists, the usual manner of denoting a certain di- or trinitrotoluene being to state the position occupied by the groups.

Lamprecht is credited with the isolation of the next dinitrotoluene. This was the 1-2-5 derivative, and was discovered by Lamprecht during experiments on the action of fuming nitric acid on toluene.

The isolation of the remaining two modifications, the 1-2-3 and the 1-3-5 is somewhat in doubt. The sources of information at hand point to either Nolting and Witte or to Bernthsen as the discoverers.

In considering the history of the trinitrotoluenes, it is found that modern chemists enter the field. The first three of these modifications were discovered quite early, it is true, but the last three were discovered within the past three years, and their discovery was due indirectly to the great war. With the trinitrotoluenes, as with the dinitro-, there are possible six isomers. The most interesting of the six is the 1-2-4-6 or symmetrical



modification. Peculiarly enough, this was the first discovered, very likely because it is the modification present in the largest proportions in the nitration of toluene.

The discoverer of the symmetrical trinitrotoluene was Dr. J. Wilbrand, who, at the time of his discovery, was working at Göttingen University. Dr. Wilbrand's discovery was made in 1862 or 1863. Speaking of his research, which led to the isolation of the symmetrical TNT, Dr. Wilbrand says: "The preparation of trinitrotoluene is very easy. Toluene is heated to about boiling temperature with a mixture of fuming nitric and sulphuric acids for a day. The acid mixture is agitated with water, and the residue is crystallized after washing with water and drying with alcohol. The analysis of trinitrotoluene is:

	Calculated.	By Experiment.
Carbon.....	37.0	36.8
Hydrogen.....	2.2	2.4
Nitrogen.....	18.5	19.3
Oxygen.....	42.3	

Trinitrotoluene crystallizes in white glistening needles, which are, to all appearances, scarcely different from dinitrotoluene. This substance melts at 82° and is easily soluble in hot alcohol, but very slightly in cold. In ether it is easily soluble. Boiling alkalis react much easier with trinitrotoluene than with dinitrotoluene. From the deep red alkaline solution, acids precipitate dark flocks." (17)

The constitution and formula of trinitrotoluene was established by Claus and Becker, who, by experiment,

proved it to be symmetrical. (18) The melting-point was found to be  $82^{\circ}$ , in accordance with Dr. Wilbrand's statement. In the light of modern research, this melting-point appears too high. The correct melting-point is probably  $80.6^{\circ}$ .

The next trinitrotoluene to be isolated was the 1-2-3-6 modification. This was discovered by Paul Hepp in 1882. (19) Hepp found the melting-point of this trinitrotoluene to be  $112^{\circ}$ .

The discovery of the 1-2-3-6 compound was followed very shortly by the discovery of the 1-2-4-5 modification by Beilstein, who isolated both the 1-2-3-6 and the 1-2-4-5 isomers the same year that Hepp isolated the 1-2-3-6. Beilstein found the melting-point of the 1-2-4-5 isomer to be  $104^{\circ}$  C.

The remaining three trinitrotoluenes have been discovered in very recent times. In 1914, Giua and Molinari discovered the 1-2-3-5 modification. (20) The isolation of this compound was accomplished while the discoverers were working on an industrial problem with the oily substance resulting from the centrifugalization of crude dinitrotoluene. It will be remembered that Nolting and Witte worked with this same substance in 1885. These latter investigators overlooked this trinitrotoluene and also several dinitrotoluenes, since Giua and Molinari found the following constituents in the oil.

Mono.	Di.	Trinitrotoluenes.
1-3	1-2-4	1-2-4-6
1-4	1-2-5	1-2-3-5
	1-2-6	
	1-3-4	

Giua and Molinari give the melting-point of this trinitrotoluene as 79.5°.

The next trinitrotoluene to be isolated was the 1-3-4-5 modification. This was discovered by Korner and Contardi in 1915. (21) Under what conditions, or from what source this trinitrotoluene was discovered is not known, since the original reference is not at hand. The melting-point given by the discoverers is 97.2°.

The last trinitrotoluene, and the last of the fifteen possible nucleus-substituted nitro-derivatives of toluene, is supposed to have been discovered by Coparisow during the latter part of the year 1915. (22) The melting-point of this trinitrotoluene is 137.5°.

The history of the nitro-derivatives of toluene is a long one. There is interest at each step, however, because of the periods of time involved, and because of the great chemists who were concerned in the isolation and constitution of these compounds. The mononitrotoluenes formed the working subjects for the working out and proof of a considerable number of the basic laws of orientation; a fact which is in itself of no little interest.



## CHAPTER III

### THE THEORETICAL NITRATION OF TOLUENE

IN this discussion of the theoretical nitration of toluene, I shall make use of the ideal process—the three-stage. If either the one- or two-stage processes were substituted, there would be changes in minor points only, and I think the three-stage illustration will render the theory more clear.

The reactions of the first nitration of toluene are as follows:

First stage:



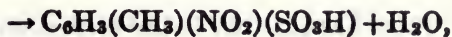
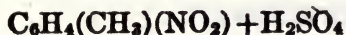
There is also a possibility that the reaction may go forward in two steps, the first step being the sulphonation of the toluene, and the second step the substitution of nitro-groups for the sulphonic groups:



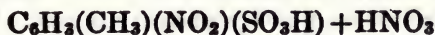
and,



The reactions of the second stage consist first in sulphonating the mononitrotoluene, and then in nitrating the sulphonate:



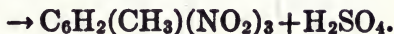
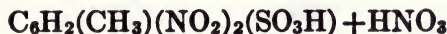
and



The third-stage reaction is similar to the second stage:



and



In each stage there may be the reactions of either previous or later stages taking place, because of the impossibility of absolute control.

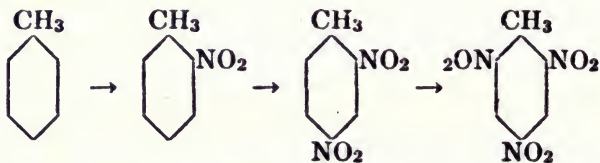
The theory that sulphonation takes place before the nitration can be accomplished may be the key to the question as to why some mono- and dinitrotoluenes are easily nitrated, and some are difficultly nitrated. The sulphonic group follows the laws of orientation perhaps more closely than almost any other group, and this explains why (assuming the sulphonation theory) dilute nitric acid will not nitrate direct, but will merely replace a sulphonic group. Therefore, if the sulphonic group is not already in place, the nitro-group cannot enter the molecule. So, if the previous



stage has resulted in the formation of isomers with the groups in such positions that the sulphonic group cannot enter the molecule easily, the isomer will be nitrated only by very strong nitric acid, or by using some special method of introducing the sulphonic group.

This solution to the question would seem to indicate that in the first-stage nitration the sulphonation does not take place, but that the toluene is nitrated directly by the use of nitric acid.

Starting with toluene, purified as is considered necessary for nitrations, the primary nitration is to mononitrotoluene. The theoretically perfect nitration would proceed in this manner:



This nitration, however, is never accomplished, for the mononitrotoluene consists of all three isomeric forms. The mononitrotoluene modifications are present in the proportion of 38 per cent para, 60 per cent ortho, and 2 to 4 per cent meta. (1) This result is exactly what would be expected, because with the methyl group in position 1, the tendency of the nitro-groups is to enter either position 2 or position 4. This fact holds true even with the more generally accepted view that the first stage of the reaction consists in sulphonating the toluene, because the sulphonic group behaves and orientates just the same as the nitro-group, and with the methyl group in position 1, the sulphonic group will also enter either position 2 or position 4. The

nitro-group can then easily replace the sulphonic group.

The formation of the small amount of meta nitrotoluene is explained thus by Holleman: (2) "It is apparent that there is an opposition between the ortho and para derivatives on one hand, and the meta derivatives on the other. Either the first two are the chief products, or the last. Concerning the temperature of the reaction, it has been proved that the quantity of the by-products is the smaller, the lower the temperature of nitration." This statement of Holleman is based on earlier work by himself, and in a paper he gives this tabulation: (3)

CONSTITUTION OF MIXTURE OF UNITS

Temp. of Nitration.	Ortho.	Meta.	Para.
Deg. C.	Per Cent.	Per Cent.	Per Cent.
-30	55.6	2.7	41.7
0	56.0	3.1	40.9
30	56.9	3.2	39.9
60	57.5	4.0	38.9

Considering, then, the mixture of mononitrotoluenes to consist of, approximately, 38 per cent para, 4 per cent meta, and 58 per cent ortho nitrotoluene; the reactions which occur on nitrating to dinitrotoluene will be investigated.

This nitration takes both the ortho and para nitrotoluenes largely to but one dinitrotoluene—the 1-2-4 modification—but a small amount of 1-2-6 is formed. The nitro-group here, as before, conscientiously follows the law of orientation and enters a position meta to

another nitro-group, but still ortho or para to the methyl group. Of course, as in the first-stage nitration, a small amount of the mononitrotoluene (especially the meta) may, under the influence of conditions concerning which we know nothing, attach nitro-groups in other than the specified positions.

By the nitration of meta nitrotoluene there is formed mainly the 1-3-4 dinitrotoluene. Some small amounts of 1-2-3 and 1-3-6 (or 1-2-5) isomers also result from this nitration. (4) In each of these cases it may be noticed that the tendency of the nitro-group is to resist the intruding prime nitro-group, which has entered the molecule contrary to the laws governing its action, because the second group will enter either ortho or para to the methyl group. These isomeric dinitrotoluenes, other than the 1-2-4, and the trinitrotoluenes together with some unchanged mononitrotoluene constitute the oil that separates from the 1-2-4 dinitrotoluene by centrifugalizing or cooling and filtering. This oil is known in Germany as "Binitrotropfol." Nolting and Witte (5) state that this oil constitutes about 7 per cent of the entire charge. Various chemists have analyzed the oil, their analyses being summarized and checked by Nolting and Witte, who found, in addition to the substances isolated by the others, some meta nitrotoluene. According to Nolting and Witte, the analysis of this oil shows the presence of 1-2-4 and 1-2-6 dinitrotoluenes, and 1-3 and 1-2 mononitrotoluenes. Giua and Molinari (6) discovered some trinitrotoluenes in the oil which were evidently overlooked by their predecessors.

Summarizing the products of the second stage, the following nitro-derivatives may appear in the mix-



ture. This summary assumes no separation of the binitrotropfol:

MNT.	DNT.	TNT.
1-3	1-2-4	1-2-3-4
1-2	1-2-6	1-2-4-6
1-4 (possibly)	1-2-3	(1-3-4-5)
	1-3-4	1-2-4-5 (1-3-4-6)
	1-2-5 (1-3-6)	(all questionable)

The amount of impurities; that is, products other than 1-2-4 dinitrotoluene, amounts to from 7 to 8 per cent.

The third stage is much more complicated than either the first or the second, on account of having so many things with which to deal. Possibly by considering the action of each compound separately, the result will be made more clear.

### MONONITROTOLUENES

1-3 nitrates to 1-3-4 DNT (possibly further nitrates to 1-3-4-5 TNT) (7);

Also 1-2-3 DNT (possibly further nitrates to 1-2-3-4 TNT) (8);

Also 1-2-5 DNT (possibly further nitrates to 1-2-4-5 TNT) (8);

1-2 nitrates to 1-2-6 DNT (9) } (Both possibly further nitrated to  
also 1-2-4 DNT (10). } 1-2-4-6 TNT).

### DINITROTOLUENES

1-2-4 nitrates to 1-2-4-6 trinitrotoluene (10);

1-2-6 " 1-2-4-6 " (9);

1-2-5 " 1-2-4-5 " (8);

1-3-4 " 1-2-3-4 " (also possibly 1-3-4-5) (7);

1-2-3 " 1-2-3-4 " (8).

(The German theory of nitration, advanced by Hepp, Escales, etc., and the Italian theory, which is supported by Giua, Molinari, Coparisow, and others; differ at this point. The Germans assert that 1-3-4-5 TNT is formed from 1-3-4 DNT, while the Italian theorists state that this is impossible. The statements given in substantiation of both theories are quoted at the end of this chapter.)

The trinitrotoluenes remain unchanged upon attempts to further nitrate, unless too strong a nitrating mixture is used. In this case they may be oxidized to trinitrobenzoic acids or to tetranitromethane. (11)

All of the lower products of nitration must, of necessity, be included in the products of the third-stage nitration, because a small amount of any or all of these may have escaped nitration in all three stages. There is no reason to suppose that any one of the nitration reactions may have proceeded to completion, with the possible exception of the nitration of 1-4 mononitrotoluene. This particular nitrotoluene is the most easily nitrated of the entire number, and from all reports, is never found in the finished product. (12)

Summarizing the products which *may* be found in the crude trinitrotoluene, the following formidable list appears:

MNT.	DNT.	TNT.
1-2	1-2-4	1-2-4-6
1-3	1-2-6	1-2-3-4
	1-2-5 (1-3-6)	1-2-4-6 (1-3-4-6)
	1-3-4	1-3-4-5
	1-2-3	

Tabulating the above summary in the order of nitration, and in view of the two theories advanced for the nitration, the following tables result:



## GERMAN

MNT.	DNT.	TNT.
1-2	{ 1-2-4 1-2-6 }	1-2-4-6
1-3	{ 1-3-4 1-2-3 1-2-5 }	{ 1-2-3-4 1-3-4-5 1-2-3-4 1-2-4-5 }
1-4	{ 1-2-4 1-2-6 }	1-2-4-6

## ITALIAN

MNT.	DNT.	TNT.
1-2	{ 1-2-4 1-2-6 }	1-2-4-6
1-3	{ 1-3-4 1-2-3 1-3-6 }	1-2-3-4 1-2-3-4 1-3-4-5
1-4	1-2-4	1-2-4-6

The differences in these two schemes are self evident. The Italian theory is probably correct, in that much more is known about the behavior of the various nitrotoluenes on nitration than was known when the German theory was proposed. In defense of his theory, Hepp states as follows:

"The theory is, that by nitration of meta nitrotoluene not less than five of the possible six trinitrotoluenes are formed. Beilstein and Kuhlberg hold that a trinitrotoluene is formed whose melting-point is 76 to 80°. They themselves doubt the constitution of this compound. 'Possibly,' they conclude,

'the small amount of substance we had was a mixture.' The truth is, we have succeeded in demonstrating that from a mixture of the nitration products of meta nitrotoluene at least two trinitrotoluenes may be isolated. . . . The first of these is a difficultly soluble compound having a melting-point of  $104^{\circ}$  C. The second, which I shall designate as the beta compound, is an isomer of the first, and melts at  $112^{\circ}$  C." (13)

Giua's statement is much more brief and to the point. He says:

"The direct nitration of toluene can give but three trinitrotoluenes, these are the 1-2-4-6, the 1-3-4-6, and the 1-2-3-4. Only through dinitrotoluidin can the other three be formed. (14)

## CHAPTER IV

### THE MANUFACTURE OF TNT

THE complete manufacture of trinitrotoluene involves the several processes of nitration, separation, washing, crystallization and possibly purification. The experimental stage has been passed in every one of these various divisions in the manufacture of this product, until the modern plant runs as smoothly as a well-oiled machine. The apparatus necessary to carry on any one or all of the steps in the manufacture of TNT is now well standardized, and many excellent machines are on the market for accomplishing the end toward which every manufacturer works—a pure product. A detailed description of the necessary apparatus will not be gone into, but a brief outline of the requirements to be fulfilled by the various machines will be given in their respective places.

The first step in the manufacture of TNT is the nitration. This reaction is carried out in a large vessel called the nitrator. This nitrator is generally a cylindrical kettle or tank, built of either an acid-proof cast metal or of boiler plate. The material of which the nitrator is built should be thoroughly tested with the acids of various concentrations met with in the manufacture of the product. The nitrator must be well equipped with cooling coils and heating coils so placed that the temperature of the reacting mixture

responds instantly to the operation of these coils. The cooling is effected by the circulation of cold water through one set of coils, and the heating coils must be supplied with either superheated steam, or steam under pressure. Some attempts have been made to build a nitrating kettle with but one set of coils, this set serving for both heating and cooling. So far as I am aware, there has never been a really efficient nitrator yet built along the above line. The trouble with this type of machine is that when cold water is wanted, it is wanted quickly, and sufficient time to manipulate the several valves necessary on the above type of machine is not to be had. In addition to the temperature control coils, the nitrator must be equipped with a good agitating apparatus. This agitator is just as necessary as the water and steam coils, and, through keeping the mixture of toluene and acid uniform, aids in maintaining the temperature level. The manufacture of TNT is essentially a problem in temperature control. After the nitration is complete, the rest of the process is easy. In order to check the operator of the nitrating kettle it is well to install a recording thermometer in each unit. This eliminates error, and causes the operator to be more careful, because he knows that a mechanical watch is being kept on his work.

I have noticed a tendency in quite a number of TNT plants to perform the nitration in a rather slipshod manner, and on remarking concerning it this reply was made: "Well, its cheaper to use a little less acid in the nitration and purify the product afterwards." This policy is very bad, it is both expensive and non-efficient. It must be remembered that while TNT is



comparatively safe, it is made primarily to *explode*. Now, the more care taken with the manufacture of TNT—the less explosions *in* the plant, and the more explosions *out* of the plant.

There are three general processes for the nitration of toluene to TNT. These are the one-stage, the two-stage, and the three-stage. All of these are being used at present in North America, but the three-stage seems to have the greatest preference. As the names imply, the process involves either one, two or three separate nitrations to carry the toluene to TNT. In some respects, the names "one-stage," "two-stage," etc., are misleading, because in every preparation of TNT, whether it be by the one-stage, the two-stage or the three-stage process, there are three distinct nitrations. With the one-stage process these three nitrations are all effected with the one acid mixture and without separation of the nitro-derivatives and the spent acid until the TNT is completed. Similarly, the two-stage and the three-stage processes accomplish the same thing in either two or three different steps, each step necessitating separation of the spent acid, and the addition of fresh acid. It must not be supposed, however, that the entire amount of the toluene is converted to mononitrotoluene before any of the mono-is nitrated to dinitrotoluene, or that all of the mononitrotoluene is nitrated to dinitrotoluene before the di-is nitrated to TNT. This ideal result is not obtained with even the three-stage process. No matter which of the three processes is used, there will always be more or less impurities existing at each stage in the form of higher or lower nitration products.

The toluene which is to be used as the raw material

in the manufacture of TNT must be very pure. The standard specifications now current in the United States are as follows:

"The first drop must distill not below 108° C.

"95 per cent of the entire sample must distill within 2°.

"The dry point must be below 112° C."

In addition, the toluene must be practically free from olefines or members of the di-olefine series. This demands that the toluene be washed several times with concentrated sulphuric acid to remove these compounds. The laboratory test for olefines consists in agitating some of the toluene with a certain percentage of concentrated sulphuric acid. If olefines are present, the acid layer will acquire a yellow to red color. This color must not be deeper than whatever shade the certain plant has adopted as its standard. The comparison standard colors consist of definite concentrations of solutions of potassium dichromate, chromic acid, etc.

The presence of olefines is dangerous because these substances form nitro-compounds in the nitration process, and these compounds are rather unstable. A fire or even an explosion may possibly result if the toluene is not freed from them. The presence of members of the aliphatic or paraffin series is not nearly so detrimental as the presence of the olefines. These compounds do not react on nitration, and with the three-stage process they may be removed after the nitration to mononitrotoluene.

As stated in Chapter III, the ideal nitration of toluene to TNT would be toluene to 1-2 nitrotoluene, to 1-2-4 dinitrotoluene, to 1-2-4-6 TNT. But this

is never accomplished. It is approached most nearly with the three-stage process, in which process purification is possible at each step. In order to compare the three processes, an outline of each is given.

**NOTE.**—The acid mixtures given are approximate only. Each plant has determined just which mixture will give the best results, some of these mixtures varying as much as 10 per cent. A statement of the exact analysis of the mixed acid is therefore impossible.

**The One-stage Process.** In the one-stage process, but one acid mixture is used. This mixture consists of 75 per cent sulphuric acid, and 25 per cent nitric acid. The usual charge for this process is in the ratio of one part toluene to twelve parts mixed acid. Each kilogram of toluene requires, therefore, 3 kilograms nitric acid and 9 kilograms sulphuric acid.

The toluene is added to the acid in the one-stage process. The termination of the inlet pipe is in a kind of well at the bottom of the nitrator, and the toluene is nitrated before it can separate and spread about. During the addition of the toluene the temperature must not rise above 30° C. This addition requires from two to two and one-half hours. After the addition is complete, the temperature of the mixture is raised to 90 to 95° C., by means of the steam coils. This temperature is maintained for two hours, during which time the mononitrotoluene is nitrated to dinitrotoluene. The temperature is then further increased to 120°, and is "cooked" for an additional two hours. The nitration is now considered finished, and the charge is ready for separation, washing, and graining. In many chemical plants a chemist tests the charge of TNT, and the time of the final cooking is determined by the solidification point of the mixed TNT and acid.



This principle of chemical control is adopted sometimes in the two- and three-stage processes as well as in the one-stage process. The yield of TNT by the one-stage process is 1.9 kilos per kilo toluene used.

**The Two-stage Process.** There are two possible modifications of the two-stage process:

1. Nitration from toluene to MNT; separation and purification of the mononitrotoluene, and nitration to TNT.

2. Nitration to dinitrotoluene, separation of this product from the spent acid, and further nitration to TNT.

The second modification has been practically discontinued in this country, and will therefore not be discussed.

The first stage of the other modification of the two-stage process requires a mixed acid which contains 30 per cent nitric acid, 55 per cent sulphuric acid, and 15 per cent water. The proportions for the charge are one part toluene to two and one-half parts acid by weight. This process differs from the one stage in that the toluene is placed in the nitrating kettle and the mixed acid is added. The addition of the acid is carried out at a temperature not exceeding 40° C., and consumes one and one-half hours. The charge is then heated to 60° for one hour, and the mononitrotoluene is separated from the spent acid. At this point of the process various procedures are adopted. The mononitrotoluene may be washed and distilled, or it may be separated from the impurities present by solution. There has been much discussion as to whether or not mononitrotoluene can be safely distilled. Recent investigations on the subject indicate



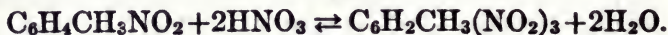
that it can be safely distilled providing there is no trinitrotoluene present. In every case, however, the distillation should be made under reduced pressure, as this lessens the danger from explosions.

Following the purification of the mononitrotoluene, or in case no purification has been made, following the separation from the spent acid, the mononitrotoluene is placed in the nitrator and is sulphonated with an amount of sulphuric acid equal to three times the weight of the mononitrotoluene. This requires about one-half hour. The reaction mixture is then heated to  $70^{\circ}$  and mixed acid containing 50 per cent each of nitric acid and sulphuric acid, equal in weight to the sulphuric acid used for sulphonating, is added through a period of one hour. After the addition is complete the charge is cooked at a temperature of  $120^{\circ}$  C. for two hours, then separated, washed, etc.

The amount of acid necessary in the two-stage process per kilogram toluene is 5.6 kilos sulphuric, and 2.2 kilos nitric. The yield of TNT per kilo toluene is 1.99 kilos.

A two-stage process has been proposed by Langenscheidt similar to the one outlined above, the main difference being that the final cooking is done at  $140^{\circ}$  C. Humphrey has made an especial study of this process, and makes certain recommendations concerning its use. (1) He recommends Langenscheidt's process, but his investigations have shown that better yields of TNT are produced by operating at a somewhat lower temperature ( $120$  to  $125^{\circ}$ ) than  $140^{\circ}$  as prescribed by Langenscheidt, and maintaining the lower temperature for a longer time than that specified for the high temperature. The proportions of acids to toluene were

such that the water concentration in the final mixture was about 4.4 per cent. The experimental data indicate that the yield of TNT at a given temperature is not a function of the water concentration of the reaction mixture as assumed from



In his discussion Humphrey makes perfectly clear the point that the above statement does not apply to either very low or very high water concentrations, because experiments have shown that with a very high water concentration the nitro-group enters the side chain of the toluene molecule, while with a low water concentration, oxidation products, such as trinitrobenzoic acids, result.

E. J. Hoffman, (2) has made a study of the effects caused by the addition of the toluene to the acid, and vice versa. In his experiments with the two-stage method (nitrating first to mononitrotoluene and then to TNT), he used an acid mixture of one part nitric acid (gravity 1.42) to two parts sulphuric acid (gravity 1.84). When the toluene was added to the acids the yield was 60 per cent mononitrotoluene and 40 per cent dinitrotoluene. On the other hand, when the acids were added to the toluene very little dinitrotoluene was formed. The temperature was more easily controlled in the first procedure, in which the toluene was added to the acid. Providing the nitration product is to be further nitrated to TNT, the presence of the dinitrotoluene is not objectionable. Hoffman's yield with this method was 75 per cent of TNT with a melting-point of 78 to 80° C.

**The Three-stage Process.** The first-stage acid for this process is composed of 70 per cent sulphuric acid, 15 per cent nitric acid, and 15 per cent water. The acid is run into the toluene, the addition generally taking about two hours. The temperature during the addition of the acid must not rise above 30° C. The proportion of acid to toluene is three to one. Following the acid addition the temperature is raised to 60° C., and is held at this point one and one-half hours. The spent acid is then separated, and the mononitrotoluene is either purified and nitrated to dinitrotoluene, or the nitration is made without any purification other than the separation of the spent acid.

The acid used in the second stage contains 60 per cent sulphuric, 25 per cent nitric, and 15 per cent water. The acid is added to the mononitrotoluene at 75° C., one and one-half hours being consumed in the operation. After this addition has been made, the charge is cooked at a temperature of 90° for one and one-half hours. Then the spent acid is separated, and the dinitrotoluene is ready for centrifugalization, or nitration to TNT without purification.

The first step in the third stage is the sulphonation of the dinitrotoluene. Oleum (fuming sulphuric acid) is used for this purpose in the majority of plants. The acid may be added very rapidly in the third stage, since the temperature is 90 to 100°. The acid analysis shows 50 per cent each sulphuric and nitric. When the addition is complete, the temperature is raised to 120° and the charge is cooked for one and one-half hours. The nitration is then supposedly complete, and the TNT is separated from the acid, and is ready for washing. The yield of TNT per kilo toluene is



2.2. The total acid necessary is 2 kilos nitric and 5 kilos sulphuric per kilo toluene.

The German process of manufacturing TNT is of interest at this point, since the manufacture of this product originated in this country. The two-stage process is the one in greatest use in Germany, and in many plants the mononitrotoluene is separated, one of the isomers being used in the dye plants, while the other two are nitrated further to TNT. The first stage of the German process consists in placing 90 liters of toluene in the nitrating kettle and adding an equal volume of nitric acid (gravity 1.25) at a temperature of 30° or lower. By using this acid alone, the Germans claim that the separation of the ortho and para mononitrotoluenes is effected more easily, and that little or no TNT is present. The para isomer is the one used for dyestuffs, and it is separated from the ortho and the small amount of meta by cooling the mixture to 10° C. At this temperature some of the para mononitrotoluene separates out and may be filtered off. If a complete separation is desired, a vacuum distillation of the mixture must be carried out. For nitration to TNT only, no separation of the three mononitrotoluenes is necessary.

The second stage of the German process is very much like the American. The mononitrotoluene (500 kilograms) is placed in the nitrator and sulphonated with 1400 kilos sulphuric acid at a temperature of 60 to 70°. Then a mixture of 700 kilos of 100 per cent sulphuric acid and 700 kilos 48° Bé. nitric acid, is run in. The mixture is agitated until a sudden drop of the temperature indicates the end of the reaction of nitrating the mononitrotoluene to dinitrotoluene. The



temperature is then raised to 120°, and held at this point until the charge is finished as indicated by the control analyses.

In some parts of Germany trinitrotoluene is made from dinitrotoluene, which occurs as a by-product in various processes of the manufacture of other materials. In such a case, the dinitrotoluene is melted, sulphonated with one and one-fourth its weight of oleum, nitrated with three-fifths its weight of nitric acid at temperatures varying from 100 to 130°, and finally separated from the spent acid, washed and crystallized.

A good comparison of the three processes used in the United States may be obtained from a summary of these processes:

	One Stage.	Two Stage.	Three Stage.
Acid, nitric.....	3	2.2	2
Acid, sulphuric.....	9	5.6	5
Yield (kilos. TNT per kilo. toluene) ..	1.9	1.99	2.2
Time (hours).....	7	6-7½	7-8

From this summary, it is apparent that the three-stage process necessitates the use of less acid—and therefore less loss of TNT by solution—but consumes more time than the other two processes. The problem of the chemical engineer is therefore to determine the best equilibrium for the conditions present in his particular plant. This calculation necessitates a knowledge of the “plant-hour” value, together with the costs of acids, toluene, and other materials, the cost of denitration of the spent acid, and the concentration of sulphuric acid. But, as a general rule, in considera-

tion of the higher grade of product turned out, the three-stage process may be said to be the best.

Many engineers have investigated to the extreme the conditions necessary for the best yields and the best product possible in the manufacture of TNT. Much credit is due one of these investigators, M. Coparisow, because of the light his research has thrown upon the nitration of toluene, and the cure for the troubles encountered in this reaction. A summary of Coparisow's work is given here, it being taken from a recent article. (3)

"The mineral matter present during the process of nitration may act either as a catalyst or as a chemical reagent, and this action may explain some of the curious occurrences in the course of a nitration. Furthermore, when mineral acids act upon the metal parts of the apparatus, hydrogen may be set free, and may reduce some of the nitro-compounds. Under the working conditions amino groups may be diazotized yielding cresols and nitrocresols, whose salts are highly explosive, and this action may explain some of the heretofore mysterious accidents in TNT plants. These may be obtained as by-products, through the action of the hydrogen, and the oxidizing action of the nitric acid itself."

"1. Trinitrobenzoic acid and tetranitromethane. These result from oxidation in case of overheating or pressure. The intense odor of the tetranitromethane is sometimes observed in the factories, but the trinitrobenzoic acid, owing to its solubility, generally escapes detection."

"2. Phenolic compounds. These, like cresols, may result from the reduction of the nitro-compounds by the

nascent hydrogen which is generated by the action of the acids upon the metal of the nitrator."

"3. Sulphonic acids. These compounds may result when the quantity of sulphuric acid is too great; i.e., when the mixture of acid contains too much sulphuric acid in proportion to the nitric acid."

In the process of the manufacture of TNT, Coparisow points out the following as being matters requiring particular care and watchfulness:

"1. The amount of nitric acid used must exceed the theoretical amount necessary by at least one-half molecule."

"2. The extent of the nitration should be regulated more by the concentration of the acids, the temperature and the duration of the nitration than by the actual quantity of nitric acid present."

"3. The reaction product should not be kept in contact with the spent acid longer than is absolutely necessary."

"4. The concentration of acid and the nature of the material in the plant should be such as to reduce their action on one another to a minimum."

"5. The raw materials must be pure."

Coparisow further states that disposal may be made of the residue from the mother liquor—which residue consists of a complex mixture of various dinitrotoluenes and trinitrotoluenes—by nitrating this with a mixed acid containing only 15 per cent nitric acid. By this method, a "liquid TNT" is obtained, which has considerable power, and has the property of gelatinizing collodion cotton, the same as nitroglycerine does. This liquid product is used in the manufacture of gelatinized explosives.



Following the nitration of the TNT, either one of two processes may be followed. The first of these processes consist in "blowing" the charge of TNT plus the spent acids to a separating pan, where the charge is allowed to cool. On cooling, the TNT crystallizes out, and so separates from the spent acid. Water is usually added to the mixture when it is blown, in order to more completely precipitate the TNT from the acid solution. McHutchison and Wright (4) have investigated the minimum amount of water necessary to completely separate TNT from the mother liquor in order to avoid unnecessary expense in the recovery of the spent acids. It was found that the maximum precipitation of TNT occurred on the addition of the acid to 4-5 volumes of water. A greater dilution than this, or the addition of the water to the acid was found to be less effective. Following the separation, the spent acid is drawn off to a tank, and may either form the basis for the new nitrating acid, or may be sent to the reclaiming plant for purification. The TNT is transported to the washing plant by either manual labor, or by melting and blowing through pipes or troughs.

The second method of disposing of the completed nitration mixture consists in cooling the products while still in the nitrating kettle, and thus forcing out the TNT from its acid solution. This procedure, of course, results in more dissolved TNT in the spent acid, but the time saved in the separation is very great, since the crystallization in pans requires about four days, while the nitrator separation requires but a few minutes. The nitrator separation is used especially in plants where the spent acid goes into the next charge of



nitrating acids. Thus, the TNT in solution in the spent acid is reclaimed, so the percentage dissolved does not matter.

Even after this separation of the spent acid, there still remains a considerable amount of acid in the TNT. In order to obtain a marketable product, this acid must all be washed out. To perform this operation, the TNT is blown from the separating pan or, if the separation was made in the nitrator, from the nitrator to the washing tanks. The washing is accomplished by means of hot water (85 to 90° C.) Seven or eight changes of water are necessary for the complete removal of the acid.

The washing of TNT was originally for the sole purpose of removing the acid and rendering the TNT neutral to litmus. This process has been extended and elaborated upon, until to-day, in a modern plant, the primary steps in the actual purification of the TNT are carried out in the washing kettle. Various chemicals have been tried in solution in the wash water. The one great success in this line is sodium sulphite. Besides acting as a neutralizing agent to the acid, the sodium sulphite liquor exerts a solvent action on the lower nitration products of toluene, and thus serves to remove some of these impurities from the symmetrical trinitrotoluene. The usual manner of using the sodium sulphite wash is to give first about four washes with hot water, then two washes with sodium sulphite liquor, which contains 20 kilograms sodium sulphite per 1000 liters water. This chemical wash is followed by a slightly acidified water wash, and then with two more pure water washes. Various other chemicals, such as sodium carbonate, sodium bicarbonate, etc.,

have been used with more or less success. It has been found that these more distinctly alkaline salts tend to darken the TNT, and also tend to render it unstable. There are, in fact, some sodium salts of TNT which explode as low as  $160^{\circ}\text{C}$ .

The washing of TNT is, in short, a chemical engineering problem which often taxes to the limit the resources of the engineer. Practice has proved that the most efficient washing apparatus is the most simple in construction. As a matter of fact, the more simple the entire TNT plant, the better the product, and the most efficient the operation of the plant. One type of washer, a very complicated piece of apparatus, built of iron, containing a lead lining, and well supplied with baffle walls, interior wells, and valves and syphons galore, was at one time in use at a certain plant. This machine was a model of the designer's art, but was absolutely useless for the washing of TNT, since the charge generally finished up by solidifying in the various valves, wells, and syphons in and connected with the machine. This necessitated dismantling the whole apparatus, and the cleansing of each individual valve and well with live steam. Plain wood tanks have now replaced this machine, and are washing the TNT perfectly, the entire tank costing less than a new lead lining for the old type apparatus, and lasting from two to three times as long. The agitation of the TNT and water in this wood tank is done by means of compressed air or steam entering through small holes in a pipe running lengthwise on the bottom of the tank.

Since TNT is appreciably soluble in hot water, the wash water from the washing machine contains a comparatively large amount of dissolved TNT. In

order to reclaim this dissolved material the wash water coming from the washers is run through a series of tanks containing baffle walls to force the water to travel a considerable distance. This is known as the "labyrinth." Here the water cools, and the TNT is thrown out of solution. These labyrinths are cleaned out periodically, and the recovered TNT is melted, sieved, and if necessary treated with a nitrating acid and finished in the ordinary way. In some cases this reclaimed TNT (sometimes of inferior quality) is mixed with good TNT ("blending") and is thus disposed of. The conscientious inspector of TNT will not allow this practice unless done under his personal supervision. Blended TNT possesses certain characteristics that pure TNT does not possess, and may thus be detected.

Following the washing, the TNT is crystallized or "grained." From the washing tank or kettle the molten TNT is run by gravity into the crystallizing pan. This apparatus consists of a water-jacketed horizontal pan, in the center of which is set a vertical shaft carrying a brass or bronze arm. This shaft may be driven by either overhead or bottom drive. The under drive is preferable from the standpoint of safety, because in this manner of drive, all belts, gears and motors are placed underneath the pan where the workmen cannot come into contact with them. The under drive furthermore lessens the possibility of contaminating the TNT, which is being crystallized in the pan, with dropping oil or grease from the belt or gears, such as might occur if the drive were of the overhead type. The arm which is attached to the revolving shaft should clear the sides and bottom of the pan by at least  $\frac{1}{8}$  inch.



This is necessary to prevent friction between the arm and the pan, and the possibility of ignition of the TNT. The arm should be set in a sloping position with the slope downward in the direction of rotation. This slope causes the TNT to climb over the arm, and greatly facilitates the graining of the material.

A second method of reducing the TNT to small particles, and which is, as yet, quite new, depends upon the rotation of a drum in the molten TNT. As the drum revolves, a thin layer of TNT adheres to it, and is scraped from the drum by a knife after about one-half revolution. This machine decreases the time necessary for the crystallization greatly. The process is known as "flaking."

The completion of the crystallization marks the end of the process of manufacture of crude TNT. The only operation left is the screening. This is done by shoveling the TNT directly from the crystallizing apparatus into an oscillating screen having 10 to 30 meshes per inch. The TNT passing through the screen is packed into boxes of 100 pounds each.

One of the problems confronting the pioneer chemical engineers in the explosive field was the disposal of the spent or waste acid from the nitrations. The analysis of a typical spent acid shows the following composition:

Nitric acid .....	3-12%
Water.....	10-30
Organic matter.....	$\frac{1}{2}$ -3
Sulphuric acid.....	Balance

The disposal of this acid in the earlier plants was accomplished by sending the acid directly from each nitra-



tion to the spent acid tank, and from this place to the denitrifying plant. Modern practice utilizes the spent acid from one stage as the basis of the nitrating mixture for the next preceding stage. This re-use is along certain lines that are developed by the individual plant. This method of using the spent acid over again possesses the following advantages:

1. The saturation of each spent acid with organic matter lessens the loss of the TNT by solution.

2. A uniform spent acid is discarded by the nitration plant, thus enabling the denitrating plant to adopt a standard practice, and to treat each batch of acid the same.

The first step in the reclaiming of the spent acid is the cooling and filtering of the acid. This removes a large part of the organic matter. The removal of the organic matter is very important, especially so if the recovered nitric acid is to be used in the manufacture of ammonium nitrate. Foreign material in the nitric acid may result in an explosion. In the United States alone, at least one explosion is known to have been caused by such contamination.

Following the removal of the organic matter, the acid goes to the denitrating plant. Here the nitric acid is separated from the sulphuric acid by blowing air and steam through the mixture. The weak nitric acid resulting from the solution from the denitrating towers is used, as stated above, in the manufacture of ammonium nitrate.

The reclaiming of the waste acid has been the object of several patents granted in the United States and foreign countries, the medium of separation being solvents, for the most part. A British patent (5),

granted in 1914, separates the nitrotoluenes contained in the waste acid by washing the acids with toluene or a nitrated toluene which has been nitrated to a lower degree than that of the products to be removed. If the process be carried out at a suitable temperature, the toluene or nitrotoluene used for the extractant undergoes nitration in the process. Fresh nitric acid may be added to the waste acids for this purpose.

Another process of extracting the organic matter from the waste acids by solvent means was patented in 1915. (6) This process is made continuous by running together the waste acid and solvent, in suitable proportions, into a mixing tank, while maintaining the appropriate temperature and pressure. The mixture flows from the mixing tank through an overflow pipe into settling tanks, where the liquids divide into layers, the nitrotoluenes formerly dissolved in the acids being now dissolved in the solvent. Suitable solvents mentioned in the process are toluene, mononitrotoluenes, etc.

A distillation process is interesting because of its uniqueness. In the operation of this process (7) the waste acid is evaporated in a suitable container, and the organic substances are removed from the gas and vapors by passing these vapors through a chamber over water. The part not absorbed by the water in this chamber passes out into a condenser. The solidified organic matter collects in a readily accessible chamber, and is removed from time to time.

A peculiar use is made of the spent acid in some parts of Russia. (8) The waste acid from the manufacture of TNT contains 62 to 72 per cent sulphuric and 2 to 3 per cent nitric acid. This is used to prepare super-

phosphate from the Russian phosphate rock. The superphosphate thus prepared is said to be much more dry and more pulverulent than that made with sulphuric acid alone.

After the separation of the nitric acid from the solution, there remains a mixture of sulphuric acid and water. This is concentrated by running slowly through a series of pans, called a "cascade," which are heated from beneath. Various other patented processes are now coming into use for concentrating sulphuric acid solutions. The acid coming from the concentrating plant is mixed with oleum to further reduce the water content, and may be used in nitrating mixtures again. Another use for the acid as it comes from the concentrating house is in the manufacture of nitric acid.

Another problem which the engineer must meet is that of transferring the TNT after it has been completed by nitration to the various other stages of the manufacturing process. With the toluene, acids and other raw materials this is comparatively easy, since these are in the liquid state. TNT, however, will solidify at  $80^{\circ}$  C. and must be kept above this temperature if it is to be blown through pipes. Blowing consists in running the TNT in a molten state into a strong box called a "blow-case," and then, by means of compressed air, forcing it out through steam-jacketed pipes. Considerable difficulty is experienced with this method of transportation, because the TNT solidifies in the pipes seemingly without the least reason. When such an occurrence takes place, it is necessary to either wait a considerable time until the TNT melts, which delays the process; or else a section of the pipe must be cut out, and the TNT removed mechanically. One very



good plan to overcome this difficulty is to run the TNT through very short pipes, by gravity, or where a short pipe is not feasible, a trough may be made, and surrounded by steam pipes embedded in asbestos cement or sand. Should the TNT solidify through accident, the trough can be readily cleaned out without delay or inconvenience.

The oily substance which separates on the second stage of the three-stage process, called by the Germans "binitrotropf," is quite indifferent to attempts made to nitrate it. The problem has been solved in Italy, according to Giua, in this manner: (9)

The oil is treated with an anhydrous acid mixture, within very narrow limits (1 : 2). With this treatment, a product is formed, having a melting-point of 66° C., and which can be separated from the oily and more difficultly nitrated portion by cooling to 40°, and allowing the oil to drain off. A second nitration will yield a product which, on being washed, melted and neutralized, melts at 80° C. This "tropf" oil has always been regarded as useless in Italy, but in Germany, where alcohol is used for crystallization, "tropf" oil is the starting-point for much of the TNT produced. A single nitration of the oil does not give a utilizable TNT if the latter is not crystallized from some solvent, because 5 to 7 per cent of the oil remains unnitrated under ordinary conditions. The use of alcohol as a solvent from which to crystallize the TNT is prohibited in Italy, because of the high tax on alcohol. Denatured alcohol cannot be used, because the pyridine, which is used as a denaturant, darkens TNT. For this reason the TNT industries in Italy use dinitrotoluene as the starting-point, and the dinitrotoluene is



centrifuged to separate the oil. By the above method of nitrating, a great amount of this oil has been saved.

It will be seen from the foregoing description of the complete manufacture of TNT that the modern factory must be much larger than a simple nitrating, washing and crystallizing plant. The modern plant must include, besides the TNT units: (a) Plant for manufacturing nitric acid; (b) Sulphuric acid concentration plant; (c) dinitrating and filtering plant; (d) ammonium nitrate plant, or other plant to utilize the weak nitric acid that is recovered from the spent acid.

Summing up the entire process, it is one of chemical control from beginning to end—from the testing of the toluene from which the TNT is made, to the analysis of the acids recovered from the waste liquors. Chemical control cannot be emphasized too greatly, and the plant with the most highly developed chemical control is the plant that turns out the best product.

## **CHAPTER V**

### **THE PURIFICATION OF TNT**

**THE** purification of TNT, while in reality a part of its manufacture, may consist of any one of a number of methods, most of which are equally good as a means of extracting the "impurities" in the TNT. There are appearing every day new methods of purifying this substance, and the number is now too great to treat each method separately. It is thought wise, in view of the fact that a differentiation is made between crude and purified TNT, to treat the purification as a separate subject, rather than to include it in the discussion of the manufacture.

The product which results from the application of the various processes outlined in the previous chapter is known as "crude TNT." To define the word "crude" as applied to TNT is rather difficult, since a crude product is generally thought of as being a product that is contaminated with foreign substances. The purified product differs from the crude product in that these foreign matters are removed. As a matter of fact, "crude" TNT contains no real impurities, in the true sense of the word, because the impurities have been removed in the washing of the crude product. There are, it is true, other compounds of nitric acid and toluene (the lower nitration products), in the TNT, and

these are the "impurities" meant when this term is used in connection with TNT.

By referring to the chapter on "The Nitration of Toluene" it is seen that TNT may contain mononitrotoluene, dinitrotoluene and even other isomeric trinitrotoluenes aside from the symmetrical TNT. The common expression "TNT" (or its synonyms) has become narrowed down to mean that certain trinitrotoluene isomer defined as the alpha, or 1-2-4-6 isomer. The melting-point of this particular trinitrotoluene as determined by reputable authorities is 80.6 to 80.8° C. Now, if other trinitrotoluenes or any mono- or dinitrotoluenes be mixed with the symmetrical TNT, the melting-point will be either raised or lowered, according to the specific nitrotoluene present. As a general rule, the melting-point of the mixture is lower than the melting-point of pure TNT, indicating the presence of some of the mono- and dinitrotoluenes. In order to remove these compounds from the TNT, many different methods of purification are resorted to. The greater number of these methods depend upon the solvent action of some substance upon the mononitrotoluenes and the dinitrotoluenes. The more important of these methods are outlined below.

1. **The Purification by Alcohol.** The crude TNT is placed upon the filter medium of a vacuum filter. An amount of 180 proof alcohol, equal in weight to one-quarter the weight of the TNT, is added. This mixture of TNT and alcohol is then agitated thoroughly, and fresh alcohol, equal to one-half the weight of the TNT is poured in on top of the mixture. The filter pump is then started, and the alcohol is filtered off until the top level of the alcohol layer is coincident



with the top of the TNT. At this point a further amount of alcohol equal to one-quarter the weight of the TNT is added, and the filter is sucked dry. The TNT is dried by either a current of warm air, or by vacuum. In the latter case, the filter must be so arranged that a vacuum may be effected in the upper chamber.

The action of the first portion of alcohol added is to dissolve the mononitrotoluenes and the dinitrotoluenes. The second volume added dilutes this solution and dissolves any of the nitrotoluenes which escaped solution by the previous addition. The last portion of alcohol serves to dissolve out any remaining traces of the impurities, and also serves to wash the TNT.

The cost of this method of purifying TNT is rather high. Pure ethyl alcohol is preferable to denatured alcohol, because of the action the denaturing agents have on the TNT. The cost of the undenatured solvent is too high, however, to permit its use unless a well-developed plan of solvent recovery is in operation, so that practically none of the solvent is lost.

**2. Purification by Sulphuric Acid.** Hot sulphuric acid, 100 per cent concentrated, possesses the property of dissolving all three classes of the nitrotoluenes. Upon cooling such a solution, the trinitrotoluene crystallizes, but the mono- and dinitrotoluenes remain in solution. This property of sulphuric acid forms the basis of another method of purifying TNT. The solution of the TNT in the sulphuric acid is effected in steam-heated, lead-lined vats. The liquor is then filtered and cooled. The recrystallized TNT must be washed with several changes of water to remove the acid. This method



of purifying TNT yields a very light-colored product. The loss of TNT is quite high, since about one-third the total amount of TNT remains in solution. The spent acid from this purification, which contains the dissolved mono- and dinitrotoluenes may be used either as a sulphonating acid, or as the sulphuric acid portion of a nitrating acid.

A modification of the sulphuric acid process has been patented (1) when applied to a mixture of mononitrotoluenes and paraffin hydrocarbons. The nitration of the toluene is carried on carefully so as to take it only as far as the mononitrotoluene. The mononitrotoluene is dissolved in sulphuric acid, but any paraffins that may be present will not dissolve, and will form a separate layer. A separation of these two layers and the subsequent nitration of the sulphuric acid solution of mononitrotoluene yields a very high grade TNT. Thus a toluene containing a comparatively large percentage of paraffins may be utilized in the manufacture of TNT.

**3. Carbon Tetrachloride and Alcohol.** A mixture of carbon tetrachloride and alcohol exerts a marked solvent action on the two lower nitro-compounds of toluene, and this action forms the basis of a patent granted for the purification of TNT. The proportions of the solvent used vary, certain conditions requiring particular concentrations of the two solvents. For the use of this solvent an especially designed filter is needed which will allow the mixture of TNT and the solvent to be thoroughly agitated directly on the filter medium. The method of operation is practically the same as that used for the purification by alcohol alone. The vacuum filter is so arranged that when the last layer of solvent

has been added, and the filter sucked dry, the apparatus may be reversed and used as a vacuum drier. Handling of the TNT is thus reduced to a minimum. This method is said to be very efficient, the loss being only 3 to 7 per cent. The cost per kilogram TNT is reported to be about 6 cents.

**4. Purification by Sodium Sulphite.** One of the cheapest and probably one of the best methods of accomplishing the purification of TNT by solvent means is by the use of a 20-per cent solution of sodium sulphite. Various methods of using this solution have been developed, the two best of these being given:

The first method consists in agitating the TNT with the hot sodium sulphite solution until the mono- and dinitrotoluenes are in solution, then cooling and allowing the TNT to solidify in the usual way. The second method consists in adding the molten TNT to the sulphite liquor in a very fine stream. The temperature of the sulphite solution should not be so low that any of the mono- or dinitrotoluenes may escape solution, but, on the other hand, should not be higher than the melting-point of the TNT. The TNT solidifies in the form of small balls or pellets, and because of this action, the process is known as "pelletilizing." Of course, the solution used in the pelletilizing process need not be sodium sulphite, as other solutions will bring about the same result.

The use of sodium sulphite as a purifying agent for TNT always necessitates a wash with 1 or 2 per cent sulphuric acid after the sulphite treatment, in order to remove the dark color which is imparted to the TNT by the sulphite. Following the sulphuric acid wash, two fresh water washes should be given.

The sodium sulphite method of purifying TNT is very cheap; the figure given by one large producer of TNT is  $\frac{1}{2}$  cent per kilogram. This firm, it is said, obtains the sulphite from the waste liquor of the hydroxide fusion in the manufacture of phenol. Assuming the above statement to be true, the cost of purification per kilogram TNT will be somewhat higher if it were necessary to purchase the sulphite. The salt need not be chemically pure for this purpose, but it should not contain appreciable quantities of the hydroxide, carbonate or other distinctly alkaline salts, since these salts will darken the TNT so deeply that the sulphuric wash may not restore the light color.

**5. Mechanical Purification.** A very interesting method of purifying TNT is in use at the plant of one of the largest producers of TNT in the United States. This process comes nearer to that used by the Germans than does any other American process. It will be remembered that in the second stage of the nitration a mixture of mono- and dinitrotoluenes forms as an oil. The procedure involved in this method is to centrifuge the dinitrotoluene and in this manner remove this oil. It is said that the oil obtained in this process may be further nitrated to TNT, but according to Giua and Molinari, and Nolting and Witte, the oil consists mostly of meta mononitrotoluene and dinitro-derivatives of the same. Will and others insist that some of these derivatives at least are not capable of being further nitrated without undergoing decomposition, or not without great difficulty. The TNT formed by the nitration of the thus purified dinitrotoluene possesses a melting-point of  $80^{\circ}\text{C}$ .



**6. Modified Solvent Process.** Still another interesting process is a modification of the sulphuric acid solvent method. This method has gained favor with a number of manufacturers because of its time-saving qualities. The procedure with this method is to add 100 per cent hot sulphuric acid to the mixture of TNT and spent acid immediately after the nitration is completed. The mono- and dinitrotoluenes together with most of the TNT dissolve in the sulphuric acid, the mixture is cooled and filtered, and the TNT recovered. This process possesses the advantage of eliminating one washing, and is thus to be preferred to the ordinary sulphuric acid treatment as outlined above. The spent acids may be used in subsequent nitrations, and the dissolved organic matter recovered in this manner.

Many other solvents may be used to accomplish the purification of TNT. The organic solvents such as toluene, acetone, etc., find an especially wide application. The method followed with these solvents may be either a simple heating of the mixture of TNT and solvent until the impurities dissolve, followed by cooling and crystallization of the TNT, or it may be a more elaborate scheme somewhat as outlined in method 1 above. Well-developed processes have been worked out for purifying TNT by solvent means using nitrobenzene and nitrotoluene as the solvents. The solvents may be purified for further use by distillation with steam. (2)

The recovery of the solvent is a very important consideration in an efficient plant. This recovery must be carried out with a great deal of care, since the concentration of the nitro-derivatives in the solvent increases as the solvent is distilled off. If the distillation is

carried too far, the nitro-compounds may decompose with explosive violence. Two cases are recalled where explosions have resulted from an attempt to carry the distillation of the solvent used for extracting the mono- and dinitrotoluenes to a too-concentrated residue. The solubility of the mono-, di- and trinitrotoluenes in the hot solvent is naturally greater than in the cold solvent. Therefore, although the boiling solvent may exhibit no signs of being saturated with the nitro-compounds, it may be near the danger point. The procedure followed by the writer in solvent recovery is to distill the solvent until the volume of the recovered solvent is equal to one-half the volume of the solution placed in the still. At this point the distillation is interrupted, and the residue, which is twice as concentrated as it originally was, is withdrawn from the still and allowed to cool, when the excess of dissolved substances will be thrown out of solution. The mixture is then filtered, and the concentration will be just the same as at the start of the operation. To illustrate: Suppose a volume of 1000 liters of solvent saturated with 6 per cent dissolved nitrotoluenes is to be recovered; 500 liters, say, of the solvent are placed in the still, and 250 liters distilled off. The residual liquid in the still now contains 12 per cent dissolved organic matter. On cooling, one-half this solute will precipitate, and after filtering the cold mixture, the solvent concentration will be the same as it originally was, -6 per cent. The remaining 250 liters may now be mixed with another 250 liters of the fresh solution and the process continued. It is not probable that the concentration of the residue at the point where the distillation is interrupted is very close

to the decomposition point, but with the operation outlined it costs nothing to be on the safe side, and practically 100 per cent solvent recovery, barring evaporation or carelessness, may be accomplished.

The still which is used for the recovery of the solvent may be a steam-jacketed still of almost any shape for the lower boiling-point compounds. For those solvents whose boiling-point is higher than that of water a direct fired still, or one supplied with high pressure steam, is necessary. In cases where simple solvents such as alcohol or acetone are to be recovered a simple still without any column will do very nicely. If the solvent is complex; that is, if it is composed of a mixture of two or more solvents, and these solvents must be separated, a more complicated still with a fractionating column is necessary. In this period of modern engineering skill, a special still designed and built expressly for the one particular purpose for which the manufacturer desires it, can be bought for very little more than a stock still, and will perform its work much more satisfactorily.



## CHAPTER VI

### THE INSPECTION AND TESTING OF TNT

By K. K. STEVENS

**Inspection.** TNT is on the market in two grades, primarily, *crude* and *refined*. The crude has not been recrystallized from solvents, while the refined has. Of these two grades, there may be several other grades based on the melting-point (M.P.) or usually the solidification point (S.P.).

The crude TNT is the more common form in the United States and when purchased by foreign governments is shipped crude and either refined or blended with other substances. The greater bulk of TNT made, up to very recently, has been shipped crude, possibly only three plants in the United States manufacturing the refined grade in any quantity. In the different plants the product is obtained in lots of approximately 2200 pounds each, called "runs."

The specifications usually call for containers, such as cases or kegs, which hold from 60 to 100 pounds, are lined with oiled paper, and numbered as to shipment, "run" and case. The inspector may be expected to check the weights, and take samples for analysis.

**Sampling.** Samples should represent lots of 4000 pounds, and for convenience a composite sample from two runs is often taken. The cases are selected, opened,

and the samples taken from different parts of the case, mixed, and three 1-pound bottles filled; one each for buyer, seller, and referee, the latter's bottle being sealed by the buyer's inspector.

**Testing.** Color should be light yellow for crude, cream for refined.

*Comment.* The color changes rapidly when exposed to strong light, sunlight changing it from yellow to orange in fifteen to twenty minutes, although the deeper shades of yellow are not an indication of impurity. The brownish grades should be inspected, though not necessarily condemned in the crude grade without confirmatory tests.

In the refined grade the color may vary with the solvent used in recrystallizing, but should usually be of a light cream, melting to a clear light brown, not darkening appreciably at 100° C. for two hours.

**Fineness.** For crude, 90 per cent shall pass through a 10-mesh sieve. For refined, 99 per cent shall pass through a 12-mesh sieve. For exploders, all shall pass through a 30-mesh sieve.

*Comment.* The crude may contain frequently 7 to 8 per cent of lumps larger than specified, but is usually O.K., always being sieved before packing, and the lumps forming on the sides of the crystallizing tub have been allowed, intentionally or accidentally, to get in the sieved product.

**Moisture.** Moisture shall not be more than 0.10 per cent for crude or refined (some specifications allow 0.15 per cent) and shall be determined by drying 2 g. over sulphuric acid for twenty-four hours.

*Comment.* The method is efficient, and will remove as much as 30 per cent moisture in the time specified.

**Acidity.** There must be no acidity. This determination is made by shaking 10 g., melted, with 100 c.c. boiling water (distilled) allowing to cool, pouring off the water extract into a flask, and reserving; the operation is repeated with 50 c.c. distilled water, adding the second extract to the first. The combined extraction is titrated with N/20 caustic alkali, using phenolphthalein as indicator.

Other specifications less definite are as follows: Shake 5 g. with 100 c.c. distilled water in a 100-c.c. graduated cylinder one minute, adding blue litmus paper and stand thirty minutes, with occasional shaking. The paper must not show any acid reaction at the end of this time.

One specification allows 0.03 per cent acid calculated as sulphuric.

*Comment.* The method of the first specification seems better, although any sodium bicarbonate washing (not used at present) will give acid reaction at this point, whereas methyl orange will give only the mineral acids. The litmus paper shows acidity with phenolic compounds as well as acids, but if the determination is carried out as specified, there will be no color to the litmus paper, it having been completely bleached, and any acid reaction is more or less doubtful. The method may be modified as follows: Shake 5 g. with 400 c.c. distilled water one minute, *filter*, stand 5 minutes and add the litmus paper; any acid reaction will be detected in two minutes. The litmus might be used instead of titrating in the first method.

**Insoluble matter** must not exceed 0.15 per cent, as determined by boiling 10 g. with 150 c.c. of 95 per



cent alcohol, collected on a weighed Gooch crucible, washed with not more than 150 c.c. of 95 per cent alcohol, drying at 95° C. one hour and weighing.

Some specifications call for benzene as the solvent and allow 0.10 per cent for refined, 0.15 per cent for medium, and 0.20 per cent for crude.

*Comment.* The method is efficient.

Turbidity in the wash water is one cause for high insoluble matter, and another cause is allowing the TNT to stand too long in the lead-lined wash tanks, the acid attacking the lead and forming lead salts.

Ash in crude TNT must not exceed 0.10 per cent, determined by igniting 1 g. in a platinum crucible, allowing to burn slowly and igniting completely, precaution being taken to prevent loss of ash.

*Comments.* The sample should be heated, ignited directly with the flame, and allowed to burn without first melting; if melted and then heated further, the sudden combustion will expel it from the crucible.

The size of the sample should be about 2 grams, taking into consideration the low percentage of ash present.

The residue called "insoluble matter" might be conveniently used for the ash determination.

Some specifications call for sulphated ash, probably to avoid loss of potassium or sodium salts during ignition.

Ash in refined TNT for exploders must be less than 0.05 per cent.

**Nitrogen.** Crude TNT must contain not less than 18 per cent nitrogen determined by the Dumas combustion method.

Refined TNT must contain not less than 18.20

per cent nitrogen determined by the Dumas combustion method.

*Comment.* The Dumas method, standard for nitrogen, requires little comment, results being very satisfactory, although it is necessary to make determinations on a substance of standard nitrogen content.

The method requires from one and one-half to three hours, and unless the chemist possesses several furnaces, not very many determinations can be made daily.

For the nitrogen determination on many organic compounds, the Gunning-Arnold method or modification of it has been used. The only modifications reported to be satisfactory for trinitrotoluene or other nitro-compounds are the zinc dust reduction by W. C. Cope, U. S. Bureau of Mines, and the use of nitron as reagent by W. C. Cope and J. Barub. (1)

The nitrogen determination is important, although if the melting-point or solidification point is up to specification, the nitrogen is seldom below.

In many instances it is common practice to average several samples for the determination of nitrogen.

**Diphenylamine Test.** Crude TNT shall contain no products which will give the nitric acid reaction with a sulphuric acid solution of diphenylamine. The determination is made by shaking with 50 c.c. distilled water in a graduated glass-stoppered cylinder, standing fifteen minutes, filtering and testing a few drops of the filtrate by adding to the diphenylamine solution. No nitric acid reaction should be obtained.

*Comments.* The blue color characteristic of this reaction is readily recognized and the test is extremely delicate.

Care must be taken that vessels are free from traces of nitric acid or nitrates.

Since other oxidizing agents, such as chlorine, chlorates, bromates, etc., will respond to this test, it is of more value, as a negative test, and fairly positive, because the oxidizing substances mentioned are not likely to be found in trinitrotoluene. A pale blue color is not confirmative; the color should be a deep blue.

**Melting-point.** The melting-point of crude TNT must be  $75.5^{\circ}\text{C}$ . or higher.

**NOTE.** This is the mean, some specifications calling for a melting-point of  $74.5^{\circ}\text{C}$ . others  $76.5^{\circ}\text{C}$ .

Medium TNT must have a melting-point of  $79.5^{\circ}$  to  $81.5^{\circ}\text{C}$ .

Refined TNT for exploders must melt from  $80^{\circ}$  to  $81.5^{\circ}\text{C}$ .

*Comments.* Methods for obtaining melting-points are not usually given in the specifications, but it is absolutely necessary that a definite procedure and definite apparatus be agreed upon. The following points should be taken into consideration: calibration and stem correction of thermometers, size of tubes, amount of substance taken, rate of melting and vessel of liquid to be used as bath.

The following is given by H. B. P. Humphries, engineer:

**Apparatus and Method.** A beaker of 1500 c.c. capacity should be filled three-quarters full of distilled water, heated by an adjustable Bunsen burner, arranged with a mechanical stirrer with the center of the blade level with the thermometer bulb, clearing it by  $\frac{1}{2}$  inch.



The thermometer should be graduated in tenths of a degree, and lowered so that the bulb is one-third the height of the beaker from the bottom and 1 inch from the side.

Tubes should be made from thin walled 6-inch by  $\frac{1}{2}$ -inch test tubes drawn out into  $1\frac{1}{8}$  inch internal diameter, cut into 3-inch lengths, and sealed at one end.

Set stirrer going and heat rapidly until temperature is about  $15^{\circ}$  below the melting-point. Meanwhile introduce a  $\frac{1}{4}$  to  $\frac{3}{8}$ -inch column of the powdered sample (previously dried to remove moisture) into a tube and tap and tamp down gently. Attach the tube to the thermometer by a rubber ring so that the center of the column of material is level with the center of the thermometer bulb, and replace thermometer as before. Reduce the heat so that the temperature rises  $1^{\circ}$  in two or three minutes. The slower rate should be adopted if several determinations are to be made at the same time.

*Readings.* Note the temperature when:

- (a) The first globule of melted material is observed;
- (b) The material is half molten and half unmelted;
- (c) The melting is complete and the clear liquid is obtained in the tube.

Record these readings, and call (b) the uncorrected melting-point.

**Corrected M.P.** Correct the readings for exposed mercury stem as follows: While the thermometer is registering the approximate melting-point, place a drop of melted diphenylamine on the stem and allow to flow down. For a small distance above the water surface the diphenylamine will remain molten; above

this it will solidify. Note the point separating the solid from molten diphenylamine.

Then, if  $N$ -number of degrees of mercury stem exposed above this point.

$T_a$  surrounding air temperature, and  $T_m$  melting-point, the correction is,  $N(T_m - T_a) \times 0.000154$ .

Add this correction to the recorded temperature (b) for the corrected M.P.

The grading of the TNT being almost entirely dependent upon this determination, the method should be carefully followed.

*Comments.* The tubes above mentioned seem too large in diameter, and a tube 1 mm. or less in diameter would give a result closer to the real melting-point.

One quarter of an inch of the substance is enough, because the higher the column, the more difficult it is to decide when half is melted completely since this compound does not always melt in one place in the tube, but often at the top and bottom simultaneously and it is left to the operator's judgment, at which point the reading is to be taken.

The three readings are taken as a check upon each other.

**Solidifying-point.** The uncertainty of the M.P. is avoided to a great degree, when the solidifying-point is determined. Only one set of specifications gives the method which is given by E. M. Weaver, Brig. General U.S.A. and Chief of Coast Artillery, in his book on "Notes on Military Explosives."

**Method.** Place 200 to 250 g. TNT in a dry porcelain dish of 15 cm. diameter and 500 c.c. capacity. Melt below  $90^\circ \text{C}$ ., remove heat and stir with thermometer. The temperature falls gradually until TNT

begins to crystallize, when it rises. Continue stirring until the highest temperature is reached. This is the solidifying-point.

*Comments.* This determination is more apt to give consistent results, and is simple enough so that the different operators usually check closely.

It is more accurate, since a larger sample is used, and the point of taking the reading more defined than in the M.P. determination.

The above method is followed, without adhering to the size of the dish. The majority of chemists use a smaller dish, or test tubes and beakers without varying results.

Although the M.P. and S.P. are generally considered the same, there is some difference, reports from different chemists showing the S.P. to be in some instances higher and in others lower than the M.P. Some report identical results for the two.

The writer (Mr. Stevens) has noted that where the M.P. was higher the TNT had been dried at 50° C. and where lower, the undried sample had been used. Further evidence is necessary for a decision on this point.

Stability tests are not usually required on crude material, although some specifications have required it on refined as follows:

About 3 g. of the substance is placed in a 6-inch test tube having a strip of potassium iodide starch paper suspended on a glass hook which passes through the stopper. The tube with contents is placed in a bath and heated to 65° C., for from fifteen to thirty minutes (depending on specification). No blue color showing presence of nitrous acid should develop.



This last is the "Abel" heat test, usually used on less stable nitro-compounds.

Since the above paper was written, many short cuts and improvements have been made in the methods of analysis. The more important of these are:

**Diphenylamine Test.** Much difficulty was encountered in this test, because of the low concentration of the oxidizing substances (nitric acid) and also because of the dilution of the blue color when a positive test was obtained; therefore the following modification was developed and adopted by at least one government as official.

The TNT is shaken with 50 c.c. distilled water in a stoppered cylinder, allowed to stand fifteen minutes, filtered, and 1 c.c. of the filtrate added to a similar volume of a 2-per cent solution of diphenylamine in concentrated sulphuric acid; by pouring the filtrate cautiously down the side of the tube. The two solutions should not mix, but should form a two-layer system. If any nitric acid or other oxidizing substance is present, a blue ring will develop at the junction of the two layers. This modification is more delicate than the original method, because when the two solutions are kept apart, any blue that develops may be readily seen, since it is concentrated at one point and not diffused through the solution. This modification also removes danger of bleaching the blue color by the heat caused by the mixing of water and sulphuric acid. While it is true that there is a slight amount of heat generated at the junction of the two layers, yet this heat is nothing near that which results from the actual mixing of the two solutions.

A pale blue ring is really not significant because of the extreme sensitiveness of the test. In fact water often contains sufficient oxidizing agents to produce a quite deep blue color. One case is recalled where double distilled water produced a test with diphenylamine when the test was applied in the above manner. To be absolutely sure of results, the water should be distilled once in the ordinary manner, then should be distilled with an alkaline solution of permanganate. Even with this precaution, the water should always be tested; or in other words a blank should be run along with the determination.

Another possible source of error in the diphenylamine test is in the sulphuric acid used to make the test solution. In many cases I have found the sulphuric acid to contain sufficient oxidizing substances to turn the entire test solution itself a deep blue. Obviously, such a solution cannot give accurate results. The test solution, when properly prepared is water white in color.

**Melting-point.** An excellent modification of the apparatus used for the determination of the melting-point which is described by the writer of the foregoing methods of analysis of TNT, consists in enclosing the thermometer, which of course carries the melting-point tube, in a glass tube, closed at one end and which extends into the heating bath as outlined above. This tube should be long enough to enclose the thermometer to such distance as the mercury column may rise. This procedure provides an air bath for the mercury column; the sample being included, and renders corrections for the exposed stem really unnecessary, since with this modification the correction is so small as to be negli-

gible. The adoption of the air bath for the thermometer is furthermore an assurance that the chemist will watch his determination very closely, for this reason: The temperature of the water outside the air bath may easily be 5 to 8° in advance of the temperature inside the tube. If the water is heated too fast, therefore, the temperature of the thermometer will rise speedily above the melting-point of the TNT, and this rate of rise will be too great for the operator to note the three points which determine the melting-point. The rate of rise of the thermometer is now officially  $\frac{1}{16}^{\circ}$  per minute. This insures close watch upon the part of the chemist, and if he be conscientious in his work, the various determinations will check to  $\frac{1}{16}^{\circ}$ . Furthermore, the danger of superheating is eliminated by the slower rate of heating. Concerning the three points which are taken as the melting-point reading, it has been said that these three temperatures are taken for the purpose of insuring the operator's close attention during the entire melting. One thing I have noticed is that chemists are inclined to slight the melting-point determination; that is, to perform it in a "don't care" manner. Anything or any modification that will insure the chemist's attention, while not lessening the accuracy of the method is well worth while in any laboratory.

A new test that has recently been imposed on TNT is an analysis of the ash for heavy metals, especially lead. This determination is considered necessary because of the use of TNT with picric acid. This latter explosive forms an especially unstable compound with lead, and for this reason the metal must not be present even as traces. Lead may creep into TNT through



allowing the acid TNT to stand in lead-lined tanks for a considerable period of time, or through insufficient washing. In connection with the above statement and requirement an analysis of the ash of TNT which was carried out for the purpose of determining the amount of sodium present in the ash, is interesting. It was found that some of the TNT offered for inspection was quite unstable, even exploding on attempting to ash it in the determination of the ash. It was suspected that some sodium compound of the TNT existed in the material, and that this was what was causing the trouble. The possibility of the sodium compounds remaining in the TNT from insufficient washing after the chemical wash was realized, and the determinations were carried out in such a manner as to retain all the sodium in the ash. Some difficulty was encountered from the tendency of the TNT to ignite suddenly—a miniature explosion, in fact—and blow the entire mass out of the crucible. This occurred, it was found, at a temperature of about  $155^{\circ}$  C. Therefore a very large crucible with a cover supported by a glass triangle was tried, and was found to be perfectly satisfactory. The ash analysis on two samples showed the following percentages. (See page 74.)

The various compounds of sodium are the result of the ignition (in ashing) upon the impure salts used in washing. The iron and silicon no doubt result from the action of the acid upon the nitrating kettle, which is usually of a high silicon cast iron.

The results indicate insufficient washing in both cases, and the percentage of sodium is no doubt high enough to cause the trouble encountered.

The Trauzl lead block test for TNT and other ex-

No. 1.

Sample weighed 500 grams

Ash weighed .1615 gram

Percentage of ash .0323

Compound.	Weight, Grams.	Per Cent of Ash.	Per Cent in TNT.	Weight of Na, Grams.
$\text{Na}_2\text{O}$ .....	.0088	5.45	.001780	.0065300
$\text{Na}_2\text{SO}_4$ .....	.0019	1.17	.000380	.0006052
$\text{Na}_2\text{CO}_3$ .....	.00539	3.34	.001078	.0023433
$\text{Na}_2\text{S}$ .....	.00744	4.61	.001488	.0044640
$\text{Fe}_2\text{O}_3$ .....	.07369	45.63	.014728	
$\text{SiO}_2$ .....	.06420	39.76	.012440	
Lead .....	Trace			
Undetermined .....	.....	.04		

Total weight of sodium .0139425 gram.

Per cent sodium in ash 8.67.

Per cent sodium in TNT .0028.

No. 2

Sample weighed 500 grams

Ash weighed .0335 gram

Per cent ash in TNT .0067

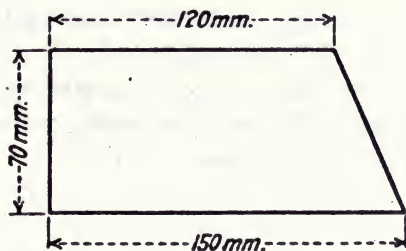
Compound.	Weight, Grams.	Per Cent of Ash.	Per Cent in TNT.	Weight of Na, Grams.
$\text{Na}_2\text{O}$ .....	.0024	7.16	.00048	.0018
$\text{Na}_2\text{SO}_4$ .....	.000549	1.64	.000199	.00018
$\text{Na}_2\text{CO}_3$ .....	.0053	15.80	.00106	.00230
$\text{Na}_2\text{S}$ .....	.00109	3.27	.000218	.00065
$\text{Fe}_2\text{O}_3$ .....	.02148	64.12	.004926	
$\text{SiO}_2$ .....	.00266	7.94	.00532	
Lead .....	Trace			
Undetermined .....	.....	.07		

Total weight of sodium .00493 gram.

Per cent sodium in ash 14.71.

Per cent sodium in TNT .000986.

plosives is a measure of the power of the explosive to enlarge a hole in a certain size block of lead. The method of performing this test consists first, in preparing lead cylinders 200 mm. in height and 200 mm. in diameter. In the axis of the cylinder is a hole 125 mm. deep and 25 mm. in diameter. These cylinders are prepared from the finest grade of refined soft lead. The casting is made in a mold which casts the central hole as well as the cylinder, thus eliminating errors from drilling. For comparative tests on various explosives, the blocks for the several tests should be made from one melt and should be cast at the same time. After casting, the blocks should be allowed to stand until they have acquired a uniform temperature of 15 to 20° C. The charge for the test is made up of 10 g. of the explosive, carefully weighed out, and then wrapped in a piece of tin foil of the size and shape shown in the illustration.



This tin-foil wrapping should be made of foil weighing 80 to 100 g. per square meter. The charge is wrapped in such a manner that a cartridge of the exact size as the diameter of the hole is formed. After the cartridge is completed, an electrically detonating charge of 2 g. is inserted in the center of it, and the whole is



pressed into place in the lead block. Fine dry sharp sand of 30 mesh or finer is tamped in on top of the cartridge to fill the hole. The charge is then fired, and after firing, the lead block is inverted and any residue is removed with a brush. The hole is then filled with water, the volume of the water measured, and the volume of the original cavity is subtracted from the final volume. The result expresses the power of the explosive.

The Trauzl test is very good for explosives of the TNT class. TNT itself gives a Trauzl test of 290 c.c. This figure will vary somewhat with the lead used, and with the operator.

Many other tests have been invented for the determination of the power of explosives. One of these depends upon the amount of sand which is crushed by the explosion of a certain amount of the explosive. Another depends upon the compression of a piece of metal by the charge of explosive being placed on top of the metal and then exploded. In all probability the Trauzl test gives as good a comparative test as any other method, and it is easily performed, is not expensive, nor dangerous.

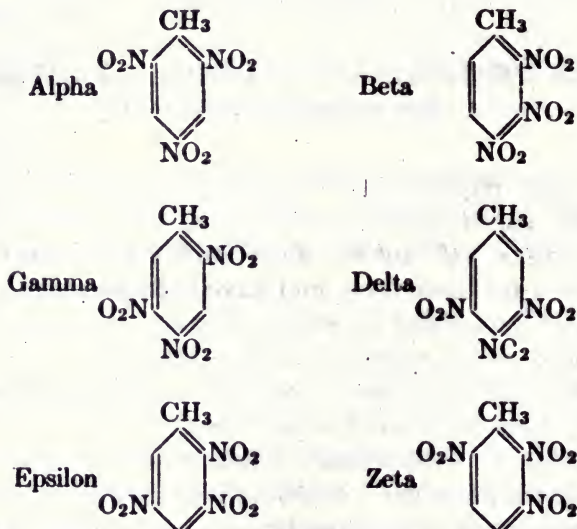
## CHAPTER VII

### THE PHYSICAL AND CHEMICAL PROPERTIES OF TRINITROTOLUENE

THE physical and chemical properties of the first three trinitrotoluenes—the alpha, beta and gamma—are quite well known, since these isomers have been known for some time, and have been prepared in sufficient quantities to enable research, which has embraced many reactions, to be carried out. The last three trinitrotoluenes—the delta, epsilon and zeta—have been discovered in too recent years to enable the scientist to reach definite conclusions concerning their chemical reactions. Practically all that is known concerning these last three isomers is the melting-point. So far as the commercial manufacture of TNT is concerned, the chemical and physical properties of the alpha, beta, and gamma trinitrotoluenes are of vastly more importance than the properties of the others, because the first-mentioned isomers constitute practically 100 per cent of the TNT. Narrowing down the relative importance still more, it is found that interest has centered on but one of the six trinitrotoluenes—the alpha. This is because the alpha or symmetrical trinitrotoluene forms about 98 per cent of the commercial product and the reactions of this product are

governed almost entirely by the reactions of the above-mentioned isomer.

The structural formula of the six trinitrotoluenes may be designated thus:



The melting-point of the alpha trinitrotoluene has been the subject of much discussion. The earlier chemists determined the melting-point of this isomer, and finally concluded that it melted at 82° C. More recent research on this subject indicates that the true melting-point is lower than that figure. Many chemists are loath to accept the lower melting-point because in several cases TNT has been prepared that melts at just about 82°. It must be remembered, however, that the commercial product contains, aside from the



alpha trinitrotoluene, varying quantities of both the beta and gamma isomers. Moreover, the melting-point of both these last isomers is considerably higher than that of the alpha. It seems logical to assume, in view of this fact, that the higher melting-point of the product is due to the presence of the beta and gamma trinitrotoluene. In any case if these two isomers were present in the form of "impurities," they would certainly exert some influence on the melting-point, and since the highest melting-point that has been obtained is  $82^{\circ}\text{C.}$ , it is entirely logical to assume that the melting-point of pure alpha trinitrotoluene is lower than this figure.

When the alpha trinitrotoluene was isolated, it was the only one of the six that was known, and even had there been present considerable amounts of the beta, gamma, or other isomers, no means was at hand for identifying them, or for separating them from the alpha. It was under these conditions that the melting-point of the first trinitrotoluene was determined, and it seems to be a very evident fact that the melting-point as determined by the earlier chemists was *not* the melting-point of pure alpha trinitrotoluene, but was a melting-point of a mixture of the isomeric trinitrotoluenes. The melting-point as determined by recent investigators varies from  $80.5$  to  $80.85^{\circ}\text{C.}$  Comey gives a melting-point of  $80.5$  to  $80.6$ . (1) Giua and Molinari state  $80.65$ . (2) Rintoul's determination gives  $80.8$  to  $80.85$ . (3) These determinations are so close together that the mean of  $80.65$  may be adopted without any serious error, even considering the true melting-point to be at the lower or higher extreme.

The complete table of melting-points of the six trinitrotoluenes is:

Alpha.....	80.65° C.
Beta.....	112.
Gamma.....	104.
Delta.....	137.5
Epsilon.....	97.2
Zeta.....	79.5

Each of the trinitrotoluenes crystallizes in definite form. The forms of the first three have been determined. No references are at hand, however, to show the crystalline structure of the last three isomers.

Alpha trinitrotoluene crystallizes in long yellow needles, which belong to the monoclinic system and the prismatic class.

Beta trinitrotoluene crystallizes in thin plates of a dazzling white color, belonging to the assymetric system.

The crystalline form of the gamma isomer, when crystallized from acetone, is rhombohedral crystals, which possess sharp edges, and which belong to the brachypinacoidal class.

The solubilities of the alpha, beta and gamma trinitrotoluenes are very much the same. There are slight variances, it is true, but these are so slight as to be of no account; for instance, all three isomers are very slightly soluble in cold water; slightly soluble in cold alcohol; and very soluble in ether, acetone, hot glacial acetic acid, etc. Alpha trinitrotoluene is very soluble in hot alcohol, while beta and gamma isomers are "moderately" soluble in the same substance. The specific solubilities of alpha trinitrotoluene are:

Cold water, .021 per cent.

Cold alcohol, 1.6 per cent.

Hot alcohol, 10.0 per cent.

Cold 100 per cent sulphuric acid, 6.6 per cent.

Hot 100 per cent sulphuric acid, very soluble.

Ether, toluene, acetone, ligroin, etc., very soluble.

**Preparation.** The alpha TNT is prepared most easily by the direct nitration of toluene. There are, of course, varying amounts of the beta and gamma isomers formed. These may be removed from the alpha isomer by the means outlined under the preparation of the beta and gamma trinitrotoluene in the following paragraph.

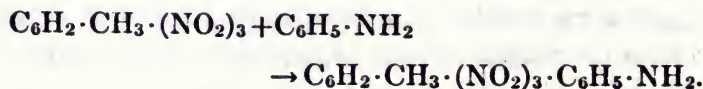
For the preparation of the beta and gamma trinitrotoluenes 100 parts concentrated nitric acid (which has been distilled from twice its weight of concentrated sulphuric acid) are placed in a flask. Two parts of meta mononitrotoluene are then added cautiously. After the first violent reaction is over, twenty-five parts of concentrated sulphuric acid are added with cooling. The mixture is then allowed to stand for twenty-four hours, being heated during this time to boiling. The boiling should not be violent, but should be rather quiet. Upon cooling the reaction mixture the beta and gamma trinitrotoluenes will separate out. The precipitated mass is well washed with hot water, and then dissolved in hot alcohol. Upon cooling, the gamma isomer crystallizes first, and thus a crude separation may be made in this fractional crystallization. To extract the beta isomer from the mixture it may be agitated with carbon bisulphide. The beta trinitrotoluene dissolves, while the gamma remains as a residue. Upon evapora-



ting off the carbon bisulphide, the beta TNT may be obtained in crystalline form. Both isomers may be further crystallized by dissolving in hot alcohol and cooling the solution slowly. The crystals thus formed are very compact and pure. Any alpha TNT may be separated from the other two isomers by fractional precipitation from alcohol, the alpha being slightly more soluble than the others.

**Chemical Properties.** There are many well-known reactions in which the three first isomers participate. Some of these reactions are little better than theoretical, and for this reason will be omitted in this discussion. The object in describing the few reactions given is to include such reactions as may form a basis for the separation of the trinitrotoluenes, or which may be of interest to the manufacturer or user of TNT.

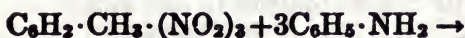
The alpha, beta, and gamma trinitrotoluenes all react with aniline, giving distinctive products. The alpha trinitrotoluene compound with aniline is the product of an additive reaction only. This compound crystallizes in long glistening needles, dark violet in color, and has a melting-point of 83° C. The crystals themselves are the same physically as these formed when trinitrobenzene reacts with aniline, and therefore cannot be used as a means of differentiating between trinitrobenzene and trinitrotoluene. The reaction proceeds according to the following equation:



Beta and gamma trinitrotoluenes react with aniline, but the product formed is not an additive compound

as in the case of alpha trinitrotoluene. Beta trinitrotoluene is rather indifferent to the presence of aniline at first. After a time the solution acquires a red color, and a vapor is given off. To accelerate the reaction, the mixture is heated in a sealed tube for four or five hours. During the heating a strong pressure develops in the tube. On opening the tube and removing the contents, it is found that two distinct substances are present: The first of these is a brownish fluid, and the other is a faintly crystalline mass which also has a brown color. Good crystals of the latter substance may be obtained by crystallizing from acetic acid, the solution being decolorized with animal charcoal and filtered before the crystallization is allowed to cool. Two crystallizations give a very pure substance, which crystallizes in short gold-colored needles, and which melts at 94° C. This substance is beta-nitrotoludin.

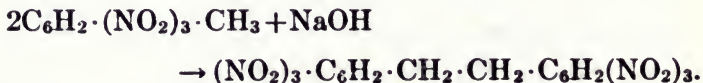
Gamma trinitrotoluene reacts with aniline readily in hot alcoholic solution. Boiling for several hours is necessary to carry the reaction to completion. Orange-colored crystals finally separate which are insoluble in cold alcohol. The first mother liquor from this crystallization reacts with hydrochloric acid giving a gas. Hepp states that this gas is very likely the result of the reaction of a diazo compound. The reactions by both the beta and gamma forms of trinitrotoluene and aniline are the same, but the beta form seems harder to start. The reaction may be represented by the following equation:



Dimethylaniline reacts with the three trinitrotoluenes in the same manner as the aniline, the resulting products, of course, being dimethyl compounds.

These reactions divide the three trinitrotoluenes into two distinct classes. Alpha trinitrotoluene constitutes the one class, in which one molecule of trinitrotoluene reacts with but one molecule of aniline or dimethylaniline while in the second class, one molecule of either the beta or gamma trinitrotoluenes reacts with three molecules of the base, forming decomposition products instead of one addition product. The property of forming addition products seems to hinge upon the symmetrical positions of the nitro-groups.

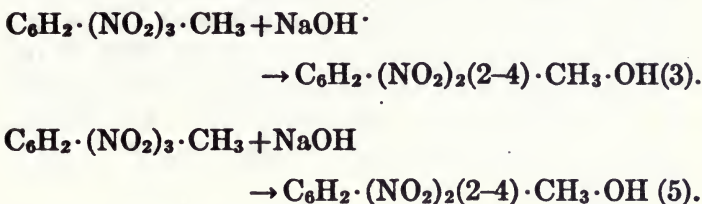
All three of the above mentioned trinitrotoluenes form compounds with the alkali hydroxides. As in the case of the aniline reactions, a distinct difference exists between the reaction of alpha trinitrotoluene and that of the beta and gamma isomers. The alpha isomer reacts with sodium hydroxide—two molecules of the former reacting with one of the latter—forming an unstable condensation product. Sodium salts of this product are very unstable, also, and are sometimes formed in the reaction:



The beta and gamma isomers react in the ratio of one molecule of the trinitrotoluene to one molecule of sodium hydroxide. Instead of the product being a condensation as with alpha trinitrotoluene; a derivative of cresol is formed. The sodium salts of the dinitrocresols have much the same properties as the



picrates, being very unstable. These reactions explain why the sodium compounds of TNT explode with such ease, and why care must be used in selecting the salt used in the washing of the crude product. The reactions of the beta and gamma isomers are, respectively:



It will be noted that in each of these reactions the nitro-group that is meta to another nitro-group and ortho or para to the methyl group does not react. This is exactly what would be expected from the orientation of the nitro-group, because the meta position to the methyl group is the unnatural position for the nitro-group, and with a basic substance such as NaOH it would be expected that it would be the one affected.

Sodium hydroxide is not the only salt that will form these unstable compounds with the trinitrotoluenes. Hepp (4) found that even the carbonates of the alkalies gave precipitations of a dark brown substance on the solution being treated with acid. He filtered this mixture, and on extracting the residue with ether obtained "a small amount of an oil, which is probably a dinitrocresol." Later Hepp identified his substance, and proved conclusively that it was a dinitrocresol.

Alpha trinitrotoluene reacts with naphthalene in benzol solution to form a needle like substance melting at 97 to 98° C. Beta trinitrotoluene and gamma

trinitrotoluene also react with naphthalene. Beta trinitrotoluene reacts rather difficultly, and the solution must be hot, and not too concentrated. The gamma isomer reacts much easier than the beta, but not quite so easily as the alpha. (5) The analysis of of the three trinitrotoluene-naphthalene compounds proves them to be addition compounds. The substance formed has the formula  $C_6H_2(NO_2)_3 \cdot CH_3 \cdot C_{10}H_8$ . The color of all the addition compounds of trinitrotoluene and naphthalene is yellowish-white. The melting-points are: Alpha, 97 to 98° C.; beta, 100° C.; gamma, 88 to 89° C.

Anthracene reacts with all of the trinitrotoluenes similarly to naphthalene, addition compounds being formed.

A further reaction with sodium carbonate has been discovered by Will. (6) He has obtained a reaction between the beta and gamma isomers and 1 per cent sodium carbonate solution in which reaction dinitrotolyloxides are formed. The salts of this compound are very explosive.

The reactions of all six isomeric trinitrotoluenes with alcoholic ammonium sulphide are known. Aside from the compounds formed, the color of the solutions are different in each case, and form a very good method of determining which trinitrotoluene is present.

Alpha trinitrotoluene gives a deep red color.

Beta trinitrotoluene gives a greenish-yellow color.

Gamma trinitrotoluene gives a blue color.

Epsilon trinitrotoluene gives a rose red color.

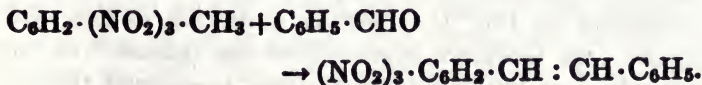
Zeta trinitrotoluene gives an orange color.

This reaction, as described by Tiemann (7), pro-

ceeds thus, to use Tiemann's words: "If trinitrotoluene (the alpha modification was used by Tiemann) is covered with strong alcoholic ammonium sulphide, a violent reaction takes place. The solution becomes first red, then seethes gently as the trinitrotoluene dissolves. Soon a mixture of sulphur and small yellow crystals separate. Boiled down the mixture leaves a residue which in dilute hydrochloric acid gives a basic compound. This compound, when precipitated by ammonia and crystallized from water, forms small red prisms, melting at 132° C. These crystals cannot be sublimed without decomposition . . . Alcohol extracts from the residue left by the hydrochloric acid treatment, a second compound, which, when freed from sulphur forms small yellow crystals. . . . It is probable that the compounds formed are respectively nitrodiamidotoluol and dinitrotoluol."

Sudborough (8) has succeeded in forming addition compounds with alpha and beta naphthylamine and alpha trinitrotoluene. These reactions take place at moderate temperatures in alcoholic solutions.

Thiele and Escales (9) report that stilbene derivatives are formed by the reaction of alpha trinitrotoluene and either benzaldehyde or piperidine. The reactions probably proceed thus:

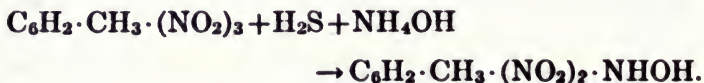


The reaction with piperidine will not form a true stilbene, but a hexahydroazostilbene. These reactions are important from a commercial standpoint, since



the stilbenes are the bases from which several important dyes are made.

Cohen and Dakin,(10) investigating more thoroughly the reaction discovered by Tiemann, to which reference is made above, identified the product from the reaction of ammonia and hydrogen sulphide on trinitrotoluene as dinitrotolylhydroxylamine. Dinitrotoluene also reacts similarly with this reagent. The trinitrotoluene reaction takes place thus:



On oxidation trinitrotoluene yields trinitrobenzoic acid. These acids are important because Meyer's esterification law was established by the preparation of the symmetrical trinitrobenzoic acid. Until 1914, but one of the acids—the symmetrical—was known. In this year Giua discovered the second and third acids, which he prepared from the beta and gamma trinitrotoluenes. The trinitrobenzoic acids are named according to the trinitrotoluene from which they are prepared.

Heating results in the ultimate decomposition of TNT. Verola (11) found, while conducting experiments to determine the vapor tension of TNT, that beginning at 160° C. a steady evolution of gas took place. He therefore investigated the behavior of the substance at varying temperatures, measuring the gas evolved. The quantity employed by Verola was 5 g. The temperatures investigated were 160°, 180°, 201°, and 217.5°. At 160° the TNT decomposed very slowly,

and a very slight volume of gas was given off. At  $180^{\circ}$  the decomposition increased, 8 cu.mm. of gas resulting. The quantity of gas increased steadily until at  $217.5^{\circ}$  the volume of the gas was 200 cu.mm. per minute. Upon heating the TNT still higher, it was found that very rapid decomposition took place at 281 to  $286^{\circ}$ . Verola determined that the reaction was exothermic.

As would be expected from the results obtained by Verola, the heating of TNT lowers the melting-point appreciably. Starting with TNT melting at  $80.75^{\circ}$  the results obtained by the same investigator summarize thus:

- 5 hours heating at  $180^{\circ}$  gave M.P. of  $78^{\circ}$ .
- $2\frac{1}{2}$  hours heating at  $201^{\circ}$  gave M.P. of  $77^{\circ}$ .
- $\frac{1}{2}$  hour heating at  $217.5^{\circ}$  gave M.P. of  $59^{\circ}$ .

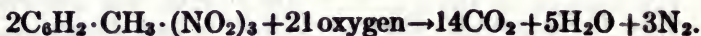
Continuing his investigations at lower temperatures, in order to find at what temperature TNT began to decompose. Verola heated TNT very long periods at lower temperatures.

- 100 hours heating at  $130^{\circ}$  had no effect.
- 80 hours heating at  $150^{\circ}$  gave a M.P. of  $80.25^{\circ}$ .
- 177 hours heating at  $150^{\circ}$  gave a M.P. of  $79.9^{\circ}$ .

From these figures it is evident that TNT is quite stable at temperatures below  $130^{\circ}$  C. The decomposition begins at  $150^{\circ}$ , being very slight at this temperature, and increases rapidly with increased temperature, until at  $281^{\circ}$  the decomposition takes place with explosive violence.

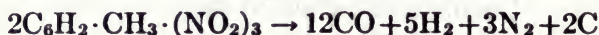
The reaction of the burning of TNT differs from the

reaction of explosion. The former reaction takes place thus:



In case the TNT is not supplied with a sufficient amount of oxygen, very little carbon dioxide will be formed. In most cases where TNT burns, the oxygen supply is insufficient, and carbon results from the combustion. When the first condition applies, the volume of the gases are 1200 liters from 1.6 kg. of TNT.

The reaction according to which TNT explodes may be represented thus:



or



according to the conditions under which the explosion takes place.

C. E. BichteI (12) has analyzed the gases from TNT under several conditions of explosion. From the complete explosion of the material under atmospheric pressure the gas gave the following analysis:

	Per Cent.
Carbon monoxide.....	70.5
Carbon dioxide.....	3.7
Hydrogen.....	1.7
Nitrogen.....	19.9
Carbon.....	4.2

Under pressure, the explosion of TNT gives a different gas, including methane and considerably more hydrogen:



	Per Cent.
Carbon monoxide.....	59.01
Carbon dioxide.....	1.93
Methane.....	1.97
Hydrogen.....	21.05
Nitrogen.....	16.05

The gases from the explosion of TNT in a lead block (from Trauzl test) upon partial analysis gave these figures:

	Per Cent.
Carbon dioxide.....	20.60
Carbon monoxide.....	46.02
Methane.....	1.40
Hydrogen.....	7.61
Hydrocarbons.....	1.08

Some authorities state that in all probability gases of entirely different constitution exist at the moment of detonation than after being cooled for analysis. The formation of methane and carbon dioxide may be due to the heat of the gases at the moment succeeding the explosion, at which moment the gases may, due to the heat, be dissociated. As the gas cools, these atoms recombine, but not in their original compounds.

The effect of daylight on TNT is very marked. A sample of light cream TNT darkens to a deep brown on exposure to strong sunlight for a few hours. This action is, in reality, a slight decomposition. Just what the products of this decomposition are, is not definitely known, but they may be separated from the TNT itself by solution in acetone. (13)

Experiments to determine the sensitiveness of TNT to shock have been carried out by von Schrotter. (14)

In his report, he tabulates the results and compares TNT to several other explosives:

Explosive.	Density.	Maximum Height at which no Explosion Occurs when a 2-kg. wt. Drops on .1 g. of Explosive.	Rate of Detonation. (M per Sec.)	Gas. Vol. (L. per Kg.)
Dry guncotton.	1.22 (compressed)	5 cm.	6583	887
Wet guncotton.	1.35 (compressed) . . . .	40	5230	901.7
Picric acid. . . . .	.85 (crystals)			
Picric acid. . . . .	1.62 (cast)	20	8183	768
Picric acid. . . . .	1.48 (compressed)			
Trinitrotoluene	.90 (crystals)			
Trinitrotoluene	1.55 (cast)	80	7620	800
Trinitrotoluene	1.62 (cast under press)			
Trinitrotoluene	1.60 (compressed)			

Von Schrotter also experimented upon the detonation of one charge of TNT by the explosion of another charge. In this work charges of 2 kgs. were used, which were enclosed in hollow metallic shells. One of these shells was equipped with an electrically fired detonator, and the second shell was placed a certain distance from the first. It was found that the TNT detonated ten times out of ten attempts at 110 cm. A heap of unconfined TNT detonated at a distance of 7.5 cm. from the prime charge.

A mixture of TNT and other substances that may be detonated by heat alone is described by Goettig. (15) The analysis of Goettig's mixture shows it to consist of: Barium nitrate, 9.83 per cent; TNT, 22.22 per cent; nitrocellulose, 67.96 per cent. The detonation of this mass may be most easily effected by an electrically heated platinum wire.

Giua has studied the physical properties of mixtures of the dinitrotoluenes and the trinitrotoluenes. He found that eutectics were formed in the ratio of three molecules of the lower nitration product to two of the higher. Langenscheidt (16) has determined the melting-points of a mixture of symmetrical trinitro- and alpha dinitrotoluenes in varying proportions. His results differ from Giua, because they indicate that the eutectic is formed in the ratio of one molecule of the lower to one molecule of the higher melting-point.

Per Cent DNT.	Per Cent TNT.	M.P.
100	0	69.5
90	10	65.5
80	20	60.3
70	30	52.8
60	40	48.0
50	50	46.0
40	60	51.5
30	70	59.0
20	80	67.0
15	85	70.0
14	86	71.3
13	87	72.0
12	88	73.0
11	89	73.5
10	90	73.2
9	91	74.8
8	92	75.0
7	93	75.6
6	94	76.3
5	95	77.0
4	96	77.7
3	97	78.3
2	98	79.0
1	99	79.5
0	100	80.4



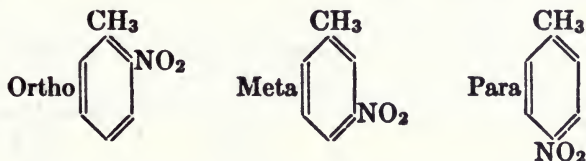
The density of TNT varies directly with the pressure applied. The following table shows the density at various pressures (17):

Pressure, Atm.	Density.
250	1.32
500	1.38
1000	1.48
1500	1.54
2000	1.57
2500	1.59
3000	1.61
3500	1.615

## CHAPTER VIII

### PROPERTIES OF THE MONO- AND DINITRO-TOLUENES

**The Mononitrotoluenes.** There are three isomeric mononitrotoluenes. The structural formulae of these are:



The melting-points of two of the mononitrotoluenes, like that of the alpha trinitrotoluene, have been under discussion for some time. Astromisslewsky (1) has made an extended study of the ortho mononitrotoluene to find out why this modification exhibits what seems to be a double melting-point, which fact had been noted by many preceding investigators. Astromisslewsky's results proved that this mononitrotoluene exists in two forms. One of these forms was designated as the alpha or "labile" modification. The melting-point of this modification was determined to be  $-10.56^{\circ}\text{C}$ . To the second form Astromisslewsky gave the name of Beta or "stable" modification, having a melting-point of  $-4.14^{\circ}\text{C}$ . The alpha form seems to go over spontaneously to the Beta modifica-

tion. Extended research indicates that the transition point is close to the melting-point of the alpha form.

Rintoul (2) has determined the correct melting-point for para mononitrotoluene. After much trouble in purification and separation from the accompanying ortho and meta forms, he finally determined the correct melting-point to be  $51.6^{\circ}\text{C}$ . and not  $54^{\circ}\text{C}$ . as was previously supposed.

The corrected boiling- and melting-points of the mononitrotoluenes are:

	Boiling-point. °C.	Melting-point. °C.
Ortho.....	223.3	-10.56 (-4.14)
Meta.....	230.0	16.0
Para.....	237.0	51.6

Specific gravities:

Ortho.....	1.168 (15 deg.)
Meta.....	1.168 (22 deg.)
Para.....	1.123 (54 deg.)

**Crystalline Form:** The crystalline form of the ortho nitrotoluene has evidently not been thoroughly investigated, since the various chemists do not agree upon this point. This is possibly due to the presence of both the alpha and the beta forms in the mixture.

Meta nitrotoluene crystallizes in monoclinic prisms, and para nitrotoluene crystals belong to the trimetric system.

**Preparation:** The preparation of the ortho nitrotoluene is most easily carried out by the nitration of

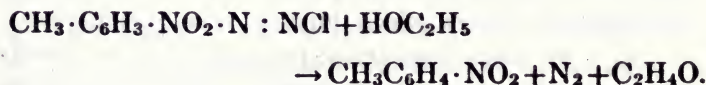
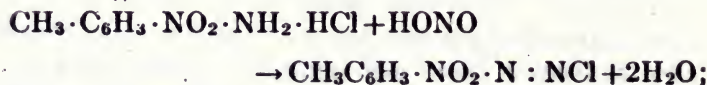
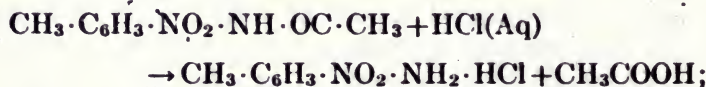
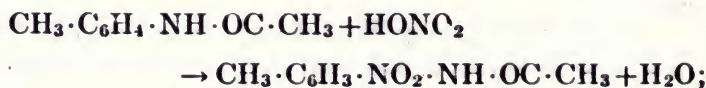
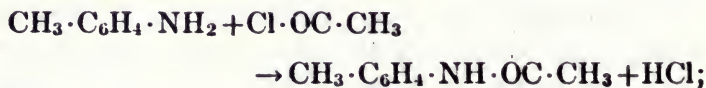


toluene. A very good mixture for this purpose is 180 parts of toluene to a mixture of 315 parts concentrated sulphuric acid (sp.gr. 1.84) and 200 parts concentrated nitric acid (sp.gr. 1.44). The toluene is placed in a vessel of suitable size and shape that is equipped with a motor-driven stirrer, and the acid mixture is added slowly. The temperature of the reaction mixture should not rise above 30° C. The mixture of nitrotoluenes from this nitration consists of all three isomers, with the ortho greatly predominating. The separation of the three isomers may be made by repeated fractional distillation, provided the nitration has been carried out at a temperature below 30°. If the temperature has risen above this point, there is danger that some dinitrotoluene or even trinitrotoluene has been formed, and upon distilling the mixture may explode.

A possibly better method of separating the isomeric mononitrotoluenes is one used by the firm of Meister, Lucius & Bruning. This consists in cooling the mixed nitrotoluenes to -4 to -10 °, and removing the liquid portion after about one-half the mixture has crystallized. The separation may be effected by a centrifuge. The liquid obtained by one crystallization is practically pure ortho nitrotoluene. The resulting mixture of meta and para nitrotoluenes may be separated by steam distillation. The para is very volatile with steam, while the meta is but slightly so.

A considerable amount of para nitrotoluene may be separated from the above residue, and easily enough so that further methods of preparation would be superfluous. A very small amount of the meta nitrotoluene is present, also, but this amount is too small to be of

any value. A much better method of preparing the meta isomer is by the successive acetylation, nitration, saponification, diazotization, and finally boiling with alcohol, of ortho- or para-toluidin. The amino group is present and thus prevents the nitro-group entering in its regulation position. Acetylation both protects the amino group, and also renders it susceptible to diazotization, which procedure is necessary for the removal of the amino group after the meta nitro-compound has been formed. The reactions in these various stages take place thus:



**Chemical Properties.** On oxidation, the mononitrotoluenes are all converted to the corresponding nitro-benzoic acid. This oxidation can best be carried

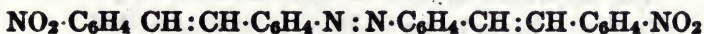
out by boiling for a long time with an alkaline solution of potassium ferricyanide.

Upon reduction, the mononitrotoluenes act differently, according to the metal used in the reduction. If iron be used with hydrochloric acid, the corresponding toluidin is produced, the reaction being analogous to the preparation of aniline. If zinc and hydrochloric acid is employed, a chlortoluidin is produced.

The reduction of the mononitrotoluenes to toluidins by the use of iron and hydrochloric acid forms the basis for a method of estimation of the para isomer in crude nitrotoluene. (3) A weighed amount of the mixed toluidins is dissolved in ether, and then ethereal oxalic acid is added. The toluidins all form compounds with oxalic acid, and all but the para compound are soluble in ether. The solution is then filtered, the residue washed with ether, then dissolved in water and titrated with N/10 sodium hydroxide, using phenolphthalein as the indicator.

The sulphonation of the mononitrotoluenes offers a qualitative test for ortho nitrotoluene, in that the sulphonation product of this isomer gives no red color when boiled with sodium hydroxide.

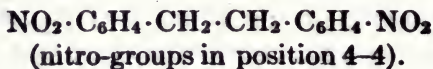
Green, Davies and Horsfall (4) have investigated the products formed when sodium hydroxide acts upon the nitrotoluenes, especially the para isomer. They have found that the first product of the reaction is a dinitrosodistilbene, which then condenses to a dinitroazodistilbene, having the following composition:



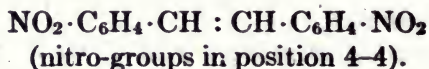
The reaction may also go to dinitrodibenzyl, accord-



ing to the temperature of the reaction and the oxidizing conditions, the formula being:



If the reaction be started cold, and gradually heated up, the product resulting is a dinitrostilbene:



The action of light on the mononitrotoluenes was investigated by Ciamician and Silber. (5) Their procedure involved the solution of the nitrotoluene in alcohol. With this solution, it was found that light transformed the nitrotoluenes into the corresponding methyl quinaldine and the toluidin. This indicated that light has a pronounced reducing action on the nitrotoluenes, reducing the nitro-group to an amino group.

The mononitrotoluenes form addition products with the inorganic salts. This property differs from the trinitrotoluenes, which form their addition products mostly with organic compounds. Walker and Spencer (6) have produced an aluminium chloride compound of mononitrotoluene, and Mascarelli (7) isolated an addition compound of para nitrotoluene and mercuric chloride, which had the formula  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3 \cdot \text{HgCl}_2$ . This substance separates from alcohol in pale yellow needles. Upon being heated, it softens at  $105^\circ$ , begins to melt at  $150^\circ$  and blackens at  $222^\circ$ . The properties of these compounds indicate that they are unstable.

An interesting application of the color reaction of nitrotoluene with sodium hydroxide is made in detecting traces of nitrotoluene in nitrobenzene. The latter substance will not give a red color with sodium hydroxide, and by standardizing the colors, the test may be made roughly quantitative. This reaction may, of course, be applied to the detection of toluene in benzene by first nitrating. (8)

Coparisow, in considering the results obtained by many investigators on the reactions of para mononitrotoluene reaches the following conclusions: (9)

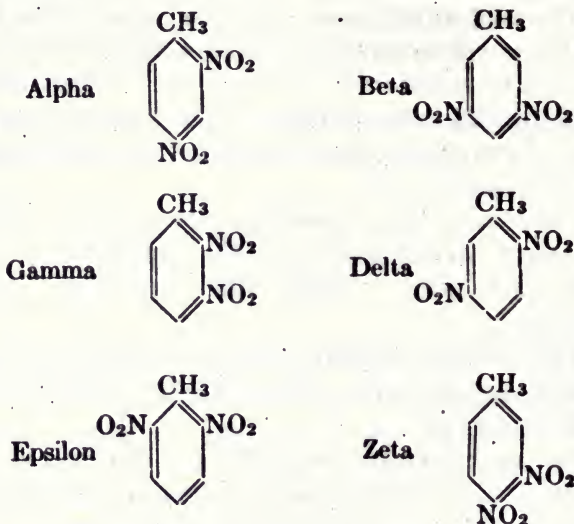
The reactive sensitiveness of nitro-groups toward alkalis increases with the increase of the nitro-groups in the molecule.

The sensitiveness and number of chemical changes is greatly augmented by the presence of an alkyl radical in the para position, facilitating, probably, the formation of nitric esters. ( $R \cdot NO(OH)_2$ ).

The reactivity of the molecule is very much increased by the introduction of electronegative groups in the ortho position to the alkyl radical.

Alkalies produce addition, substitution, and condensation products. Alkalies and alkali compounds produce red colorations with alpha trinitrotoluene. Coparisow found that when 5 c.c. of a saturated solution of potassium hydroxide in methyl alcohol, cooled in solid carbon-dioxide-ether mixture, are added to .166 g. of pure symmetrical trinitrotoluene, dissolved in a mixture of 1 c.c. pyridine and 5 c.c. methyl alcohol; the latter solution being kept cool in solid carbon-dioxide-ether mixture, the color change took place at a temperature as low as  $-65^{\circ}C$ .

**The Dinitrotoluenes.** The structural formulae of the six dinitrotoluenes are as follows:



**Melting-points:**

Alpha.....	70° C.
Beta.....	93
Gamma.....	63
Delta.....	48
Epsilon.....	61
Zeta.....	60

**Crystalline form:**

Alpha, monoclinic needles, yellow in color.

Beta, yellow needles from a mixture of acetic acid and benzol.

Gamma, hair-like needles when crystallized from dilute acetic acid.



Delta, yellow needles from ligroin.

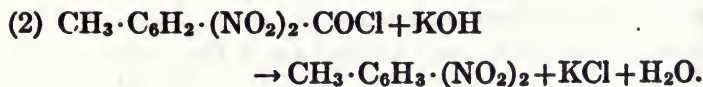
Epsilon, yellow needles from alcohol.

Zeta, very long needles when crystallized from carbon disulphide.

**Preparation.** The alpha dinitrotoluene is obtained usually by the nitration of mononitrotoluene. It may also be prepared by eliminating the amino group from nitrotoluidin, first diazotizing, then forming the hydrochloride and saponifying.

The beta isomer is formed by eliminating the amino group from dinitro-ortho-toluidin, as outlined above.

The gamma dinitrotoluene may be easiest prepared by heating 2-3-1-4 dinitrotoluic acid with dilute hydrochloric acid. The reaction goes in two steps:(10)



The delta modification may be formed from 1-4-3-6 dinitrotoluic acid as in the case of the gamma isomer. Delta dinitrotoluene may also be formed by interaction of toluquinone dioxime and nitric acid. (11)

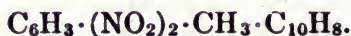
Epsilon dinitrotoluene is formed to a slight extent when mononitrotoluene is further nitrated. It may also be formed in the pure state by the elimination of the amino group fromd initro-para-toluidin.

Zeta dinitrotoluene is prepared from the nitration products of toluene.

**Chemical Properties.** The chemical properties of the dinitrotoluenes have not been investigated nearly

as thoroughly as have those of the mononitrotoluenes and the trinitrotoluenes. This is possibly because the dinitrotoluenes are merely an intermediate between the mono- and trinitrotoluenes, and are important only as such. While it is true that in some plants the dinitro-compound forms the starting point for TNT, yet in the vast majority of factories the raw material is either toluene or mononitrotoluene.

The alpha dinitrotoluene will form addition products with naphthalene and anthracene just as the alpha trinitrotoluene will do. The naphthalene product has the following formula. (12)



This same DNT may be reduced by iron and aqueous hydrochloric acid to tolylene m-diamine. Ammonium monosulphide partially reduces alpha dinitrotoluene in which reduction the para group is the one concerned. Stannous chloride and alcohol exert the same action. The product in each case is  $\text{C}_6\text{H}_3 \cdot \text{CH}_3 \cdot \text{NO}_2 \cdot \text{NH}_2$ .

Beta dinitrotoluene upon oxidation with ferricyanide forms the corresponding dinitrobenzoic acid.

Some work has been done on the reduction of the alpha and epsilon dinitrotoluenes by electrochemical means. Brand and Lolier (13) have prepared from the epsilon compound a 2-2-dinitro-6-6-azoxytoluene and a 2-2-dinitro-3-hydroxy-6-6-azotoluene. The formation is determined by the solution used. The alpha dinitrotoluene gives similar substances.

**The Omega Nitrotoluenes (Phenylnitromethanes).**  
Under various circumstances in the regulation manufacture of TNT a side-chain nitrated compound is

formed. These constitute the class of nitrotoluenes known as the omega class. The first reference to the preparation of one of these compounds is made by Holleman (14) in 1894, when he prepared an "exonitrotoluene." Hantzsch (15) and Ponzio (16) have done considerable work on the properties of the omega nitrotoluenes. The results of both these investigators indicate that these nitro-compounds are very unstable. Ponzio prepared the phenyldinitromethane, which crystallized in large prisms. The crystals melted at 79° C., and upon heating were found to decompose violently at 130° or above. The products of the decomposition of phenyldinitromethane are "red vapors and benzaldehyde." The same man prepared the potassium derivative of the above-mentioned compound, and found it to be less stable than the phenyldinitromethane itself. In fact, the alkali derivative exploded when "slightly heated."

According to Neogi and Adhicary (17) omega mononitrotoluene is readily prepared by the action of mercurous nitrate or benzyl chloride. Heim (18) concludes from a series of researches, that pure phenylnitromethane is not subject to spontaneous decomposition, but a small amount of impurities may cause such action. Korwalloff (19) has determined that this substance, on reduction, yields the corresponding aldehyde and oxime.



## CHAPTER IX

### ACCIDENTS

TNT is considered the safest explosive that has ever found a wide application in warfare. The manufacture of this explosive is also comparatively safe, as long as it is carried out with ordinary caution. There is no doubt but that in the present rush to produce TNT in the greatest possible quantities, and in the least possible time, there is a tendency to be somewhat lax in the enforcing of precautionary measures, and that there is also a tendency to disregard the chemical properties of the various products and by-products that result from the manufacture of this product. The fact that TNT is primarily an explosive, makes certain the further fact that there are certain conditions under which it must explode. It is true that not many of these conditions are known, but it certainly is not impossible that some of these conditions can be produced in the plant where the explosive is manufactured. It is no more impossible that TNT will explode under conditions concerning which we know nothing. These conditions may just as well be brought about as the first kind. To be on the safe side, then, it is up to the superintendent of a plant to be certain that no conditions exist in his plant but those under which it is definitely known that TNT will *not* explode. This will insure the safety of the men, and the safety of the plant.

Previous to 1914, there were in all less than a half-dozen accidents reported in TNT plants. Within the last year there have been not less than twenty explosions and accidents in the United States alone. It is true that not all of these have been due to the detonation of TNT, but probably every one has been due to carelessness on some employee's part. With conditions as existed previous to the war, the manufacture of TNT could be carried out with as great care as was thought necessary, but with the total rearrangement of conditions as they exist to-day, there is no doubt but that in many cases certain details which, although minor in nature, are really important, are not given the attention they require.

The pre-war accidents in which TNT was concerned were due in some cases, at least, to the action of some substance other than the TNT. For instance: In 1909 an explosion occurred in the crystallizing room of a TNT plant at Schoenbeck, Germany, in a long rotating drum which was used for drying TNT crystals. In this particular plant centrifuges were used to separate the crystals from the alcohol used for the recrystallization. It is thought that a hot bearing may have ignited the alcohol vapors in the room, thus causing the explosion. Experts differ on the subject. Some believe that the explosion was due only to a mixture of air and alcohol vapor, while others think that TNT dust was added to the explosive mixture. In either case, the TNT did not explode, since it was found that after the fire, following the explosion, was extinguished, there remained some unburned TNT in the drum. Furthermore, a wood sieve containing several hundred pounds of TNT was burned, but the TNT did not explode.

A metallic container filled with TNT was blown 300 yards, but the explosive was only slightly melted on the top. Another explosion took place in 1906 in the storeroom of the Roberite factory situated at Witten. The room was filled with TNT and ammonium nitrate. Forty-two persons were injured in this explosion.

Both of the above cases show that the explosions were not due to the detonation of TNT alone, but to the combined action of the TNT and some other substance.

Two further accidents are interesting, although not much is known concerning the conditions surrounding the explosions. In 1908 an explosion of TNT at the factory of Letsch & Co., Huddersfield, caused the death of five men. Another explosion in the washing plant of a German factory in 1912 resulted in the death of four men.

Even considering the high casualty rate of the present, the explosives manufacture has a lower injury and death rate than has railroading. Dr. W. G. Hudson, the medical director of the E. I. Dupont deNemours Co., "hit the nail on the head" in his recent paper on "Safeguards in the Manufacture of Explosives" when he said: "If explosives like dynamite, smokeless powder and TNT were made only by skilled chemists, under the best of laboratory conditions, they would seldom, if ever, cause explosion accidents. They are stable and safe explosives, and will stand a far greater degree of rough handling than the uninitiated have any idea of. But when such substances have to be produced in the immense quantities required by present conditions, ordinary labor must be used, and many of these men are unskilled and have



no speaking knowledge of English. However careful our chemists, supervisors and foremen may be, it is difficult indeed to guard against some one of these thousands becoming careless or negligent at times, and, of course, the results of an explosion are visited upon all in the vicinity."

The problem of eliminating the explosive accidents becomes then, one of making the plant fool-proof, or of educating the foreigner. The first is impossible from the very nature of the work. A foreigner—and even some Americans—may be told repeatedly to keep away from any source of nitrous fumes, for instance, but sooner or later the effect of the most stringent warning wears off. The psychology of the employee of the explosive plant is another important factor in safety work. The ordinary workman knows full well that he is employed in an explosive plant, and that his work is dangerous because an explosion may occur. Therefore at the slightest unusual noise, or at the most trivial occurrence which is out of the ordinary, he immediately suspects trouble, becomes frightened, loses his head, and often turns an absolutely harmless situation into a dangerous one. To cite an example: The chemical engineer of a certain explosive plant was one day inspecting the installation of some acid eggs that were placed in a concrete pit. He noticed that the compressed air inlet valve leaked, thus allowing air to enter the egg, forcing the acid out through the discharge pipe which had, for some reason, been disconnected about 2 feet from the egg. A drop of the acid had struck him in the face, and while wiping it off with his handkerchief, he called to a nearby workman to shut off the compressed air valve more tightly.

The workman, immediately saw a sign of an accident, became confused, and instead of turning off the air, opened the valve wide, forcing the acid charge out of the egg, and down on the man in the pit, burning him very badly.

The plant officials are thus confronted with the great problem of educating the workmen to keep a level head at all times.

Aside from accidents of the above nature, there are others the direct cause of which is carelessness on the part of foremen or superintendents, who are either ignorant of certain properties of their products, or who are negligent in the performance of their duties. One accident, due to a combination of these shortcomings, resulted from the too rapid mixing of spent acid from one stage of a nitration with fresh nitric acid to prepare the acid for the next nitration. Nitric acid on being mixed with spent acid, tends to form a separate layer apart from the spent acid unless it is thoroughly agitated. In this instance, the two-layer system formed, consequently the organic matter in the spent acid next to the layer of nitric acid was subjected to the nitrating action of the latter. As the reaction proceeded, the mixture became warm, the heat in turn accelerated the nitrating reaction and so on. With such an uncontrolled reaction taking place an explosion resulted. Nine times out of ten, the mixing of the nitric acid with the spent acid may be carried out without special precaution. The tenth time may be the cause of an explosion. In this particular plant the fortifying acid is always mixed in a particular manner. The explosion taught a lesson in the effects of disregarding minor details, and also concerning the

properties of spent acid, which should have been determined before in the laboratory.

There is surely no step in the manufacture of TNT which is entirely free from danger. Every step in the process should receive the utmost attention, and minor details should be worked out with the same care as the greater problems, rather than to "take a chance" that no accident will result.



## CHAPTER X

### TNT DISEASES

THE problem of disease incident to the manufacture of TNT has assumed great proportions in the last few years. Before the manufacture of TNT grew so large, an occasional sickness or death from poisoning caused no great comment. Now, however, with the many plants manufacturing this material, the number of men and women who are constantly becoming afflicted with diseases of various natures has grown to such a large figure that many physicians are devoting their entire time to the conquering of TNT diseases.

To give some idea of the large number of persons who are affected in one way or another, the following figures are cited: Dr. Hamilton, in May, 1916, reported 703 cases of TNT poisoning, and 33 deaths resulting from such poisoning. The Royal Society report of the same year gives 181 cases of jaundice alone, which were caused by TNT. The same report shows 52 deaths.

There has been considerable discussion among some plant officials as to why the medical fraternity is unable to check the TNT disease. I have followed quite closely much of the research work that has been done on this problem, and I am of the opinion that the physicians are doing everything in their power to obtain sufficient knowledge concerning the action of TNT so they can, with the results obtained, lay the foundation

for the treatment of disease resulting from the action of TNT on the human body. When the recentness of these diseases is considered; and when the vast amount of work necessary to be carried out with such diseases as tuberculosis, cancer, pneumonia and others, is considered, it seems that the medical profession is to be congratulated for having progressed as far as they have in the understanding of this sickness.

Many well-known physicians and pathologists have worked on this subject. Drs. More, Panton, Feldman and others have, by their researches, thrown much light on the action of TNT in the body. At the present time Dr. Samuel Haythorn, of the Singer Memorial Laboratory, Allegheny General Hospital, is engaged in a very extended series of researches to determine the various ways in which TNT gains an entrance into the body, and also to find out the effect of the TNT on the various tissues and organs in the body. The different ways in which TNT gets into the system has been investigated by Dr. More, who reaches the conclusion that the most important means of entrance is through the skin, by actual contact with the material. In order to determine whether or not TNT has gone through the system, use is made of Webster's test which detects TNT, or possibly some product of its action in the body, in the urine. Webster's test is performed by placing  $12\frac{1}{2}$  c.c. urine in a test tube, and mixing with an equal amount of 20 per cent sulphuric acid. The acidified urine is then extracted with ether, the extraction being carried out most easily in a separatory funnel, using 10 c.c. ether. The aqueous layer is drawn off, and the ether is washed with water and again separated. Five c.c. of the ether extract is

then mixed with 10 c.c. of a 4 per cent solution of potassium hydroxide in absolute alcohol. If TNT (or its product) is present, a pink color appears, which quickly changes to a purple and finally to a brown. The question as to whether Webster's test detects TNT or one of the products produced by the action of TNT upon the system has never been definitely settled.

Dr. More has experimented upon the possibility of TNT entering the body through the skin, by rubbing some of the substance upon his hand, then washing immediately. He reports that he obtained a positive Webster's test on his urine for a period of ten days. Dr. Haythorn has been unable to verify More's work, in that he has been unable to secure a positive Webster's test on his urine at all by applying TNT externally. Furthermore, Haythorn allowed the TNT to remain in contact with the skin for a considerable period of time but was still not able to obtain a positive Webster reaction. Guinea pigs whose skin had been rubbed with TNT soon developed an eruption, at first not serious, but which soon became covered with crusts.

Haythorn's next experiment consisted in subjecting rabbits and guinea pigs to the fumes of heated TNT for several hours a day for over a month. In this way the animals were under the same conditions as men in the plants who are forced to breathe fumes from washing or crystallizing apparatus, or from any source where the TNT is subjected to heat. The animals used in this test showed no Webster reaction.

Haythorn then attempted to introduce TNT by feeding the animals milk which contained dissolved TNT. The animals rapidly lost weight, became listless and soon died, one of them in three days. The



urine of these animals showed a strong positive Webster's test. The liver, spleen and kidneys of one of these animals were very dark in color, due to the breaking up of the red blood cells, and the deposition of the coloring matter in these organs.

From Dr. Haythorn's experiments, it seems that the greatest danger from TNT poisoning comes from actually swallowing the material. More does not agree with this. The effect of the TNT in the body seems to be mostly on the liver, the poison almost totally destroying the cellular portion of this organ.

Several blood tests on patients afflicted with TNT poisoning shows that the substance in many cases attacks the red blood corpuscles, depositing the coloring matter of these corpuscles in the various organs such as spleen and kidneys.

The differences in the results obtained by the work done by More and Haythorn, together with the fact that in some plants TNT poisoning is quite prevalent, while in others it is practically *nil*, has suggested that the poisonous effects may not be due to TNT itself, but to a phenylnitromethane; that is, a toluene nitrated in the side chain. It is known that these phenylnitromethanes are very poisonous. It is also known that in some cases these compounds are formed during the nitration of toluene; for instance, if the nitric acid concentration of the acid mixture becomes very low, or if the temperature rises very high. In this way, some samples of TNT may contain the toxic phenylnitromethanes, while other samples may be free from them. This would explain the difference in toxic effect of the various TNT samples, and the variation in results obtained.

There are six definite forms of TNT poisoning known:

1. *Dermatitis*, or eruption of the skin. Often called "TNT rash." This form of poisoning is caused by contact with the TNT, and may usually be cured by removing the cause.

2. *Gassing*. This condition is due more to the inhalation of the nitrous fumes which occur during the nitration of TNT than to the TNT itself. The wind passages and lungs are often badly inflamed. Many cases develop into pneumonia, while others recover after a day or two of complete rest. In any case the patient who has been "gassed" should be given attention by a physician. Ordinary first-aid methods, such as doses of dilute chloroform-alcohol mixtures, are not sufficient.

3. *Minor poisonings*, which result from the handling of TNT or receptacles which are covered with the substance. The effects differ from TNT dermatitis in that the effects are internal as well as external. The symptoms are dizziness, headache and sometimes nausea. Men or women who are new to the work, and who are not accustomed to being around TNT, are especially subject to this form of poisoning from TNT. The symptoms usually disappear after the person becomes more accustomed to the presence of TNT. Cases have been known, however, where the poisoning has developed into a more serious form.

4. *Severe Poisonings*. After the symptoms of a minor poisoning are displayed, there is a period in which the subject feels perfectly well, no effects of the TNT being noticeable. This neutral period may, in cases of extreme susceptibility, terminate in severe

poisonings. The symptoms of the more severe cases being loss of appetite, vomiting and constipation. The severe poisonings from TNT appear to be the result of a cumulative action of the poison.

5. *Toxic Jaundice.* This is the most serious form of TNT poisoning. It does not appear until at least six weeks after the exposure to the explosive. Some persons appear to be quite susceptible to the more serious forms of TNT poisoning, while others never feel anything other than the minor effects that are experienced upon the first exposure. There is yet a third class who are not affected in any way by TNT. Personally, I have often handled TNT until my hands and forearms were stained a deep golden brown, and have worked in an atmosphere filled with TNT dust for hours, but I do not recall even a slight headache or dizziness from such exposure.

Toxic jaundice is the direct result of what may be termed "TNT liver." The yellow color of the skin caused by the internal action of the TNT persists long after the stain by external contact wears off. Furthermore, the color due to jaundice affects the entire body, while the mechanical staining colors only those parts which have been in contact with the TNT. About 33 per cent of the cases of toxic jaundice are fatal.

6. *Anæmia.* This disease is the result of the action of TNT upon the erythrocytes or red blood corpuscles. These corpuscles are disintegrated, and the coloring matter is deposited in the kidneys and other organs, causing these organs to assume a dark brown or black color. As with toxic jaundice, not every person suffers the same effects. Some cases are on record where an



actual increase in the number of red blood corpuscles has resulted from TNT poisoning.

The summation of the research that has already been done on TNT poisoning indicates that the solution of the problem consists more in prevention than in treatment. The steps to be taken in prevention, which have been suggested by the British Ministry of Munitions are:

1. The employment of no persons under eighteen years of age without special permission. This insures the employment of none but mature men and women and lessens liability from carelessness or indifference.

2. The rotation of work at two-week intervals; thus removing the employee from contact with the substance periodically.

3. The use of masks, gloves, and clean-laundered overalls.

4. Large and well-ventilated workrooms,

5. The furnishing to every employee of free milk and cocoa, and a weekly medical inspection.

The wisdom of requiring the employees to drink milk has been severely questioned for this reason: Milk contains primarily fats and casein. The fats are capable of dissolving a large amount of TNT. Therefore, should any of the explosive accidentally find its way into the milk, or should there be any in the stomach through swallowing dust in the factory, this will dissolve in the fats of the milk and will be absorbed by the blood. This action has been proved by Dr. Haythorn, who has performed several experiments upon rabbits and guinea pigs with a solution of TNT in milk.

The very least that can be said concerning the toxic action of TNT is that some persons are very susceptible

to it. Minor poisonings should be treated as possible cases of severe poisonings until all doubt of the severe poisoning has been removed. A medical corps of sufficient size to afford constant medical supervision of the force of employees should be in constant attendance at the plant. In this way any slight poisoning or sickness will be checked before it has a chance to develop into a more serious form.

The first part of the paper is devoted to a general discussion of the problem of the origin of life. It is shown that the problem is one of the most important and most difficult in the history of science. The second part of the paper is devoted to a discussion of the various theories of the origin of life. It is shown that the most plausible theory is that of the origin of life from non-living matter. The third part of the paper is devoted to a discussion of the various theories of the origin of life. It is shown that the most plausible theory is that of the origin of life from non-living matter. The fourth part of the paper is devoted to a discussion of the various theories of the origin of life. It is shown that the most plausible theory is that of the origin of life from non-living matter. The fifth part of the paper is devoted to a discussion of the various theories of the origin of life. It is shown that the most plausible theory is that of the origin of life from non-living matter. The sixth part of the paper is devoted to a discussion of the various theories of the origin of life. It is shown that the most plausible theory is that of the origin of life from non-living matter. The seventh part of the paper is devoted to a discussion of the various theories of the origin of life. It is shown that the most plausible theory is that of the origin of life from non-living matter. The eighth part of the paper is devoted to a discussion of the various theories of the origin of life. It is shown that the most plausible theory is that of the origin of life from non-living matter. The ninth part of the paper is devoted to a discussion of the various theories of the origin of life. It is shown that the most plausible theory is that of the origin of life from non-living matter. The tenth part of the paper is devoted to a discussion of the various theories of the origin of life. It is shown that the most plausible theory is that of the origin of life from non-living matter.



## REFERENCES

---

### CHAPTER II

- (1) *Anallen*, 77, 216.
- (2) " 155, 1-29.
- (3) " 54, 9.
- (4) " 54, 12.
- (5) " 77, 216.
- (6) " 76, 286.
- (7) " 77, 216.
- (8) " 131, 304.
- (9) " 77, 216
- (10) " 44, 306.
- (11) *Jahres Berichte*, 22, 360.
- (12) *Anallen*, 155, 2.
- (13) " 128, 178.
- (14) *Berichte Chem. Gesell.*, 3, 202.
- (15) *Jahres Berichte*, 22, 360.
- (16) *Anallen*, 172, 221
- (17) " 128, 178.
- (18) *Berichte*, 16, 1596.
- (19) *Anallen*, 215, 375.
- (20) *Chem. Zentr.* 1914, II, 762.
- (21) *Atti. R. Accad. Lincei.*, 24, I, 888.
- (22) *Marshall*, "Explosives," 260-231.

### CHAPTER III

- (1) *Proc. K. Accad. Metensch*, Amsterdam, 1908, Vol. XI, 248.
- (2) *Organic Chemistry* (Holleman) Ed. 1910, 486.
- (3) *Proc. K. Accad. Metensch*, 1908, Vol. XI, 248.
- (4) *Rec. trav. Chim.*, 27, 208.
- (5) *Berichte*, 18, 1336.
- (6) *Chem. Zentr.*, 1914, II, 762.

- (7) *Annalen*, 215, 344.
- (8) *Berichte*, 1913, 558.
- (9) *Anallen*, 217, 208.  
*Anallen*, 225, 384.
- (10) *Berichte*, 18, 306.  
*Anallen*, 44, 307.
- (11) *Berichte*, 1914, 707.
- (12) *Anallen*, 155, 1-29.
- (13) *Anallen*, 215, 344.
- (14) *Gazz. Ital. Chim.*, 45 II, 32-44.

#### CHAPTER IV

- (1) *Journal Ind. and Eng. Chem.*, 8, 998.
- (2) *Met. and Chem. Eng.*, 14, 467-8.
- (3) *Chem. News*, 112, 247.
- (4) *J. Soc. Chem. Ind.*, 34, 781-2.
- (5) British Patent No. 23,181, Nov. 27, 1914.
- (6) British Patent No. 15,445, Nov. 2, 1915.
- (7) U. S. A. patent No. 1,149,585, Aug. 10, 1915.
- (8) *Ann. Inst. Agron. Moscow*, 19, 56-9.
- (9) *Z. ges. Schiess-Sprengstoff*, 10, 109-11.

#### CHAPTER V

- (1) U. S. A. patent, 1,225,321, May 8, 1917.
- (2) British patent, 7047, May 11, 1915.

#### CHAPTER VI

- (1) *Journal Amer. Chem. Soc.*, 39, 504-14.

#### CHAPTER VII

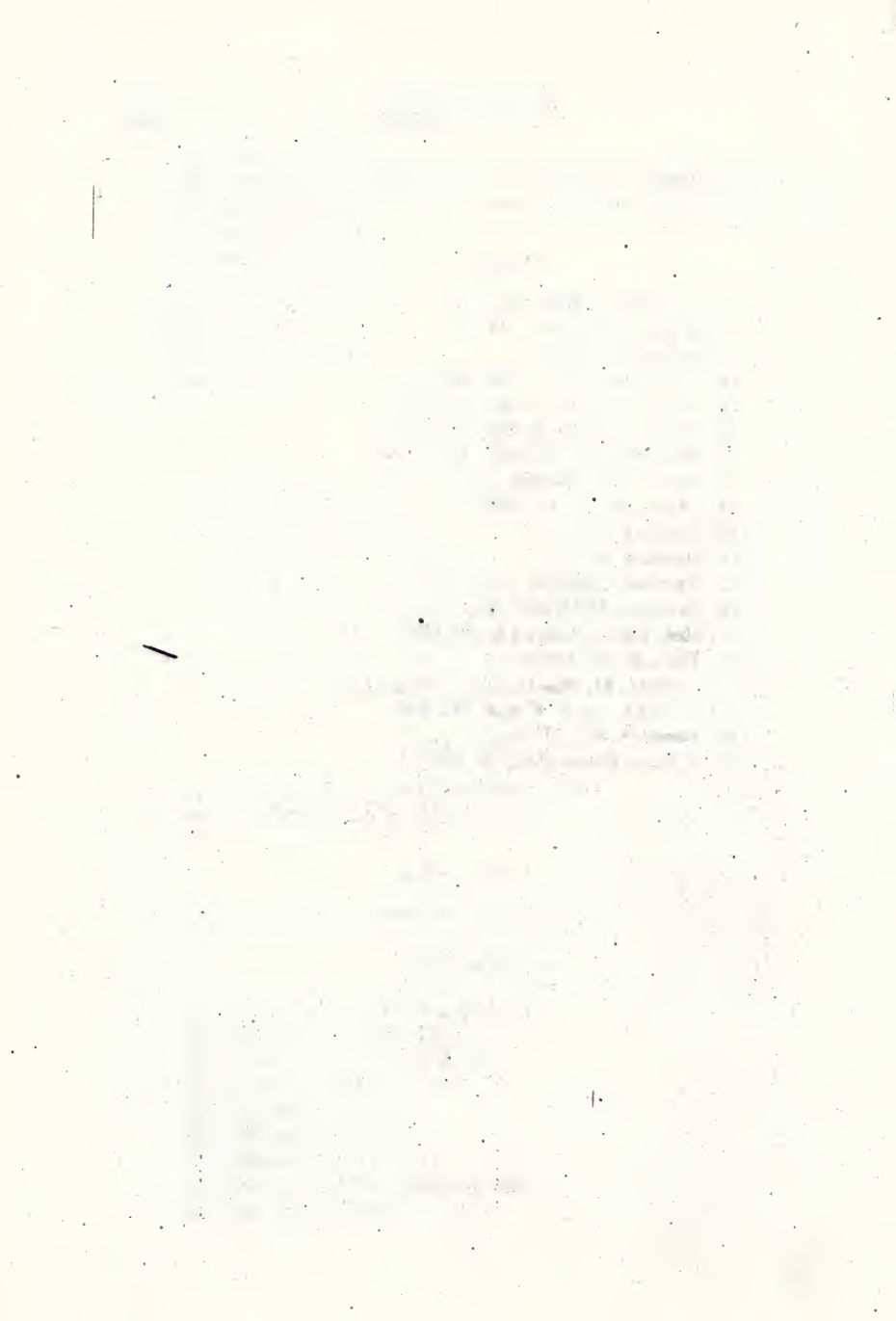
- (1) *J. Ind. and Eng. Chem.*, 1910, 103.
- (2) *1st Scienze Let.*, 46, 1913.
- (3) *J. Soc. Chem. Ind.*, 1915, 60.
- (4) *Anallen*, 215, 344.
- (5) *Anallen*, 215, 370.
- (6) *Berichte*, 1914, 704.
- (7) *Berichte*, Vol. III, 217.
- (8) *Trans. Lon. Chem. Soc.*, 79, 350.
- (9) *Berichte*, 34, 2842.

- (10) *Trans. Lon. Chem. Soc.*, 1903, 527.
- (11) *Mem. Poud. Saltpetres*, 16, 40-51.

## CHAPTER VIII

- (1) *Zeit. Phys. Chem.*, 57, 341.
- (2) *J. Lon. Chem. Soc.*, 34, 60.
- (3) *Berichte*, 36, 4260.
- (4) *Abst. Chem. Soc.*, 1907, 2076.
- (5) *Atti. R. Accad. Lincei*, 14, II, 199.
- (6) *Trans. Lon. Chem. Soc.*, 1903, 1108.
- (7) *Atti. R. Accad. Lincei*, 14, II, 199.
- (8) *Chem. Zeit.*, 30, 295.
- (9) *Chem. News*, 112, 283-4.
- (10) *Berichte*, 22, 2681.
- (11) *Berichte*, 21, 428.
- (12) *Annalen*, 215, 370.
- (13) *Berichte*, 40, 3324 et seq.
- (14) *Rec. Trav. Chem.*, 14, 121-130.
- (15) *Berichte*, 32, 607.
- (16) *Gazetta*, 31, 133.
- (17) *Zeitschr. Anorg. Chem.*, 69, 270.
- (18) *Berichte*, 43, 3417.
- (19) *J. Russ. Chem. Soc.*, 30, 960.





# INDEX

---

## A

	PAGE
Accidents.....	106
Acidity in TNT, determination of.....	63
Acids, table of.....	39
Action of inorganic salts on MNT.....	100, 101
of light on MNT.....	100
of light on TNT.....	91
of mineral matter on nitration.....	40
of nascent hydrogen on nitration.....	40, 41
Alkali carbonates, reaction with TNT.....	85, 86
hydroxides, reaction with TNT.....	84
Aluminium explosive.....	4
Ammonium nitrate.....	47
sulphide, reaction with TNT.....	86, 88
Analysis of gases from the burning of TNT.....	90
of gases from explosion of TNT.....	91
of TNT.....	62
Anæmia from TNT.....	117
Aniline, reaction with TNT.....	82, 83
Ash in TNT, determination of.....	64

## B

Benzaldehyde, reaction with TNT.....	87
Benzoen.....	6
Binitrotropfol.....	24, 50
Blending.....	45
Blood, effect of TNT upon the.....	115
Flow case.....	49

	PAGE
Boiling-point of the mononitrotoluenes .....	96
Burning of TNT, reaction of .....	90

## C

Cheddite .....	5
Chemical control .....	34, 51
properties of dinitrotoluenes .....	103
of mononitrotoluenes .....	98
of trinitrotoluenes .....	82
Color of TNT .....	62
Constituents of crude TNT .....	26
Constitution of TNT .....	17
Crystalline form of dinitrotoluenes .....	102
of mononitrotoluenes .....	96
of trinitrotoluenes .....	80
Crystallization .....	45

## D

Denitration of spent acid .....	47
Density of TNT .....	94
Detection of toluene in benzene .....	101
Determination of para nitrotoluene .....	99
Detonators .....	4
Dimethylaniline, reaction with TNT .....	84
Dinitrocresols .....	85
Dinitrotoluenes, action of naphthalene upon .....	104
and TNT, eutectic mixture .....	93
chemical properties of .....	103
crystalline form of .....	102
history of .....	15
melting-points of isomeric .....	102
nitration of .....	21, 26, 27
oxidation of .....	104
preparation of various .....	103
products of nitration of .....	27
reduction of .....	104
structural formulæ of .....	102



	PAGE
Dinitrotoluidoxides.....	86
Diphenylamine test.....	65, 70
Disease in TNT plants, prevention of.....	118
Donarite.....	5
Dracyl.....	8

## F

Effect of breathing fumes from burning TNT.....	114
of breathing fumes from nitration.....	116
of heat on TNT.....	88
of swallowing TNT.....	114
of TNT on the blood.....	115
of TNT on the skin.....	114, 116
Exonitrotoluenes.....	105
Explosion of TNT, reaction of.....	90
Explosions.....	106
Explosive tests on TNT.....	92
Eutectic mixture of DNT and TNT.....	93

## F

Factors affecting nitration.....	40
yield.....	41
Fineness of TNT, determination of.....	62
Flaking.....	46
Formation of DNT in first stage nitration.....	36
of phenolic compounds in nitration.....	40
of sulphonic compounds in nitration.....	41
Fortification of spent acid, precautions.....	110
Fumes from burning TNT, effect of.....	114
from nitration, effect of.....	116

## G

Gases from the explosion of TNT, constituents of.....	91
Gassing.....	116
German process of nitration.....	38



# INDEX

129

	PAGE
<b>Mononitrotoluenes, boiling-points of isomeric</b> .....	96
chemical properties of.....	98
crystalline form of.....	96
effect of temperature on formation of.....	23
history of.....	9
melting-points of isomeric.....	96
nitration of.....	21, 25
oxidation of.....	98
preparation of isomeric.....	96
products of the nitration of.....	25
reduction of.....	99
separation of.....	97
specific gravity of.....	96
structural formulæ of.....	95

## N

<b>Naphthalene reaction with dinitrotoluenes</b> .....	104
with trinitrotoluenes.....	85
<b>Naphthylamine, reaction with TNT</b> .....	87
<b>Nitration, factors affecting</b> .....	40
formation of DTN in first stage of.....	36
formation of phenolic compounds in.....	40
formation of sulphonic compounds in.....	41
ideal.....	22
Langenscheidt process of.....	35
one-stage process of.....	33
three-stage process of.....	37
two-stage process of.....	34
<b>Nitrator</b> .....	29

## O

<b>One-stage process of nitration</b> .....	33
<b>Orthonitrotoluene, test for</b> .....	99
<b>Oxidation of dinitrotoluenes</b> .....	104
of trinitrotoluenes.....	88



## P

	PAGE
Packing.....	61
Para nitrotoluene, determination of .....	99
Permonite.....	4
Phenolic compounds in nitration.....	40
Phenylnitromethanes.....	104
Picric acid.....	3
disadvantages of .....	3
sensitiveness of .....	92
Piperidine reaction with TNT.....	87
Plasteryl.....	4
Poisoning from TNT.....	112
Potassium ferricyanide reaction with MNT.....	98
Precautions in fortifying acids.....	110
Preparation of dinitrotoluenes.....	103
of mononitrotoluenes.....	96
of trinitrotoluenes.....	81
Prevention of TNT diseases.....	118
Products of nitration of dinitrotoluenes.....	27
of mononitrotoluenes.....	25
Purification of trinitrotoluene by alcohol.....	53
by carbon tetrachloride mixture.....	55
by mechanical means.....	57
by sodium sulphite.....	56
by sulphuric acid.....	54, 58

## R

Rash, TNT.....	116
Reaction of burning of TNT.....	90
of explosion of TNT.....	90
Reduction of dinitrotoluene.....	104
of mononitrotoluene.....	99
Retinaphtha.....	6
Rules for health in munition plants.....	118

## S

Screening.....	46
Separation of mononitrotoluenes.....	97

	PAGE
Shock, sensitiveness to, of guncotton.....	92
of picric acid.....	92
of TNT.....	92
Skin, effect of TNT on.....	114, 116
Sodium salts of TNT.....	44, 57, 84
Solidifying point of TNT, determination of.....	68
Solubilities of TNT.....	81
Solvent recovery, stills for.....	60
Specific gravity of mononitrotoluenes.....	96
Spent acid, analysis of.....	46
denitration of.....	47
effect of, on TNT.....	41
separation of TNT from.....	47
utilization of.....	48
Stability tests.....	69
Stilbene derivatives.....	87
Structural formulæ of dinitrotoluenes.....	102
of mononitrotoluenes.....	95
of trinitrotoluenes.....	78
Sulphonation theory.....	21
Sulphonic acids, formation of.....	41

T

Test explosive.....	76
for orthonitrotoluene.....	99
for toluene in benzene.....	101
Trauzl lead block.....	73
Webster's.....	113
Tetranitromethane.....	40
Theory of nitration, German.....	27
Italian.....	27
of sulphonation.....	21
Three-stage process of nitration.....	37
Thunderite.....	4
TNT anæmia.....	117
TNT jaundice.....	117
TNT rash.....	116

	PAGE
<b>Toluene detection of, in benzene</b> .....	101
from balsam of tolu.....	6
from coal tar.....	8
from crude wood alcohol.....	8
from dragon's blood.....	7
from pine resin.....	6
history of.....	6, 7, 8
nitration of.....	20
specifications for.....	32
synthetic.....	9
<b>Trauzl lead block test</b> .....	73
<b>Trinitrobenzoic acids</b> .....	40
<b>Trinitrotoluene, action of light on</b> .....	91
analysis of.....	62
and DNT, eutectic mixture of.....	93
blending of.....	45
constitution of.....	17
crystalline form of.....	80
crystallization of.....	45
density of.....	94
effect of breathing fumes from burning.....	114
of breathing fumes from nitration of.....	116
on the blood of.....	115
on the skin of.....	114, 116
on the system of.....	115
flaking.....	46
gases from burning.....	90
gases from explosion of.....	91
graining of.....	45
history of.....	17
inspection of.....	61
melting-points of isomeric.....	80
packing of.....	61
poisoning from.....	112
preparation of isomeric.....	81
purification of.....	52
reaction of.....	82
screening of.....	46



# INDEX

133

	PAGE
Trinitrotoluene, sensitiveness of.....	92
separation of from spent acid.....	42
solubility of.....	81
structural formulae of.....	78
washing of.....	43

## U

Utilization of spent acids.....	48
---------------------------------	----

## W

Washing of TNT.....	43
Webster's test.....	113

## Y

Yield, factors affecting.....	41
-------------------------------	----

Pharm.

7

a n

ct

p<sub>3</sub>

t

aH

sl/c

na

# A SELECTED LIST OF BOOKS ON CHEMISTRY AND CHEMICAL TECHNOLOGY

*Published by*

**D. VAN NOSTRAND COMPANY**  
25 Park Place New York

---

**American Institute of Chemical Engineers.** Transactions.  
8vo. cloth. Issued annually. Vol. I., 1908, to Vol.  
IX., 1916, now ready. each, net, \$6.00

**Annual Reports on the Progress of Chemistry.** Issued  
annually by the Chemical Society. 8vo. cloth. Vol. I.,  
1904, to Vol. XII., 1915, now ready. each, net, \$2.00

**ASCH, W., and ASCH, D.** The Silicates in Chemistry and  
Commerce. Including the exposition of a hexite and  
pentite theory and of a stereo-chemical theory of gen-  
eral application. Translated, with critical notes and  
additions, by Alfred B. Searle. Illus.  $6\frac{3}{4} \times 10$ . cloth.  
476 pp. net, \$6.00

**ASHLEY, R. H.** Chemical Calculations. Illustrated.  
 $5\frac{1}{4} \times 7\frac{1}{2}$ . cloth. 286 pp. net, \$2.00

**BAILEY, R. O.** The Brewer's Analyst. Illustrated. 8vo.  
cloth. 423 pp. net, \$5.00

**BARKER, A. F., and MIDGLEY, E.** Analysis of Woven  
Fabrics. 85 illustrations.  $5\frac{1}{2} \times 8\frac{3}{4}$ . cloth. 319 pp.  
net, \$3.00

**BEADLE, C.** Chapters on Papermaking. Illustrated.  
12mo. cloth. 5 volumes. each, net, \$2.00

**BEAUMONT, R.** Color in Woven Design. A treatise on  
the science and technology of textile coloring (woolen,  
worsted, cotton and silk materials). *New Edition, re-*  
*written and enlarged.* 39 colored plates. 367 illustra-  
tions. 8vo. cloth. 369 pp. net, \$8.00

*All prices subject to change without notice.*



— **Standard Cloths, Structure and Manufacture.** 150 illustrations, 16 plates.  $5\frac{1}{2} \times 8\frac{3}{4}$ . cloth. 342 pp. net, \$5.00

**BECKHOLD, H.** *Colloids in Biology and Medicine.* Translated by J. G. Bullowa, M.D. In Press.

**BENNETT, HUGH G.** *The Manufacture of Leather.* 110 illustrations. 8vo. cloth. 438 pp. net, \$4.50

**BERNTHSEN, A.** *A Text-book of Organic Chemistry.* English translation. Edited and revised by J. J. Sudborough. Illus. 12mo. cloth. 690 pp. net, \$2.50

**BERSCH, J.** *Manufacture of Mineral Lake Pigments.* Translated by A. C. Wright. 43 illustrations. 8vo. cloth. 476 pp. net, \$5.00

**BEVERIDGE, JAMES.** *Papermaker's Pocketbook.* Specially compiled for paper mill operatives, engineers, chemists and office officials. *Second and Enlarged Edition.* Illus. 12mo. cloth. 211 pp. net, \$4.00

**BIRCHMORE, W. H.** *The Interpretation of Gas Analyses.* Illustrated. 12mo. cloth. 75 pp. net, \$1.25

**BLASDALE, W. C.** *Principles of Quantitative Analysis.* An introductory Course. *Second Edition, revised and enlarged.* 70 illus.  $5\frac{1}{4} \times 7\frac{1}{2}$ . cloth. 414 pp. net, \$2.50

**BLÜCHER, H.** *Modern Industrial Chemistry.* Translated by J. P. Millington. Illus. 8vo. cloth. 795 pp. net, \$7.50

**BLYTH, A. W.** *Foods: Their Composition and Analysis.* A manual for the use of analytical chemists, with an introductory essay on the History of Adulterations. *Sixth Edition, thoroughly revised, enlarged and rewritten.* Illustrated. 8vo. cloth. 634 pp. \$7.50

— **Poisons: Their Effects and Detection.** A manual for the use of analytical chemists and experts, with an introductory essay on the Growth of Modern Toxicol-

- ogy. *Fourth Edition, revised, enlarged and rewritten.*  
Illustrated. 8vo. cloth. 772 pp. \$7.50
- BÖCKMANN, F.** Celluloid; Its Raw Material, Manufacture, Properties and Uses. 49 illustrations. 12mo. cloth. 120 pp. net, \$2.50
- BOOTH, WILLIAM H.** Water Softening and Treatment. 91 illustrations. 8vo. cloth. 310 pp. net, \$2.50
- BOURCART, E.** Insecticides, Fungicides, and Weed Killers. Translated by D. Grant. 8vo. cloth. 500 pp. net, \$4.50
- BOURRY, EMILE.** A Treatise on Ceramic Industries. A complete manual for pottery, tile, and brick manufacturer. A revised translation from the French by Alfred B. Searle. 308 illustrations. 12 mo. cloth. 488 pp. net, \$5.00
- BRISLEE, F. J.** An Introduction to the Study of Fuel. A text-book for those entering the engineering, chemical and technical industries. 60 ill. 8vo. cloth. 293 pp. (Outlines of Industrial Chemistry.) net, \$3.00
- BROWN, HAROLD.** Rubber, Its Sources, Cultivation and Preparation. Ill. 6 x 8¾. 237 pp. \$2.00
- BROWN, W. A.** The Portland Cement Industry. 36 illustrations. 5½ x 8¾. cloth. 168 pp. net, \$3.00
- BRUCE, EDWIN M.** Detection of the Common Food Adulterants. Illus. 12mo. cloth. 90 pp. net, \$1.25
- BUSKETT, E. W.** Fire Assaying. A practical treatise on the fire assaying of gold, silver and lead, including descriptions of the appliances used. Illustrated. 12mo. cloth. 112 pp. net, \$1.25
- BYERS, HORACE G., and KNIGHT, HENRY G.** Notes on Qualitative Analysis. *Second Edition, revised.* 8vo. cloth. 192 pp. net. \$1.50
- CAVEN, R. M., and LANDER, G. D.** Systematic Inorganic Chemistry from the Standpoint of the Periodic

- Law.** A text-book for advanced students. Illustrated.  
12mo. cloth. 390 pp. net, \$2.00
- CHRISTIE, W. W.** Boiler-waters, Scale, Corrosion, Foaming. 77 illustrations. 8vo. cloth. 242 pp. net, \$3.00
- **Water, Its Purification and Use in the Industries.**  
79 illus., 3 folding plates, 2 colored inserts. 12mo.  
cloth. 230 pp. net, \$2.00
- CHURCH'S Laboratory Guide.** A manual of practical chemistry for colleges and schools, specially arranged for agricultural students. *Ninth Edition, revised and partly rewritten* by Edward Kinch. Illustrated. 8vo. cloth, 365 pp. net, \$2.50
- CORNWALL, H. B.** Manual of Blow-pipe Analysis. Qualitative and quantitative. With a complete system of determinative mineralogy. *Sixth Edition, revised.* 70 illustrations. 8vo. cloth. 310 pp. net, \$2.50
- CROSS, C. F., BEVAN, E. J., and SINDALL, R. W.** Wood Pulp and Its Uses. With the collaboration of W. N. Bacon. 30 illustrations. 12mo. cloth. 281 pp. (Van Nostrand's Westminster Series.) net, \$2.00
- d'ALBE, E. E. F.** Contemporary Chemistry. A survey of the present state, methods, and tendencies of chemical science. 12mo. cloth. 172 pp. net, \$1.25
- DANBY, ARTHUR.** Natural Rock Asphalts and Bitumens. Their Geology, History, Properties and Industrial Application. Illustrated. 12mo. cloth. 254 pp. net, \$2.50
- DEERR, N.** Cane Sugar. 280 illustrations.  $6\frac{1}{2} \times 9\frac{3}{4}$ . cloth. 608 pp. net, \$7.00
- LUMESNY, P., and NOYER, J.** Wood Products, Distillates and Extracts. Translated by D. Grant. 103 illustrations. 8vo. cloth. 320 pp. net, \$4.50
- DUNSTAN, A. E., and THOLE, F. B.** A Text-book of Practical Chemistry for Technical Institutes. 52 illustrations. 12mo. cloth. 345 pp. net, \$1.40



- DYSON, S. S., and CLARKSON, S. S.** *Chemical Works, Their Design, Erection, and Equipment.* 80 illustrations, 9 folding plates. 8vo. cloth. 220 pp. net, \$7.50
- ELIOT, C. W., and STORER, F. H.** *A Compendious Manual of Qualitative Chemical Analysis.* Revised with the co-operation of the authors, by William R. Nichols. *Twenty-second Edition, newly revised* by W. B. Lindsay. Ill. 12mo. cloth. 205 pp. net, \$1.25
- ELLIS, C.** *Hydrogenation of Oils, Catalysis and Catalyzers, and the Generation of Hydrogen. Second Edition, revised and enlarged.* *In Press*
- ENNIS, WILLIAM D.** *Linseed Oil and Other Seed Oils.* An industrial manual. 88 illustrations. 8vo. cloth. 336 pp. net, \$4.00
- ERMEN, W. F. A.** *The Materials Used in Sizing.* Their chemical and physical properties, and simple methods for their technical analysis and valuation. Illustrated. 12mo. cloth. 130 pp. net, \$2.00
- FAY, IRVING W.** *The Chemistry of the Coal-tar Dyes.* 8vo. cloth. 473 pp. net, \$4.00
- FERNBACH, R. L.** *Chemical Aspects of Silk Manufacture.* 12mo. cloth. 84 pp. net, \$1.00
- *Glue and Gelatine.* A practical treatise on the methods of testing and use. Illustrated. 8vo. cloth. 208 pp. net, \$3.00
- FIRTH, J. B.** *Practical Physical Chemistry.* Ill. 5 x 7. cloth. 189 pp. net, \$1.00
- FISCHER, E.** *Introduction to the Preparation of Organic Compounds.* Translated from the new (eighth) German edition by R. V. Stanford. Illustrated. 12mo. cloth. 194 pp. net, \$1.25
- FOYE, J. C.** *Chemical Problems. Fourth Edition, revised and enlarged.* 16mo. cloth. 145 pp. (Van Nostrand Science Series, No. 69.) \$0.50
- FRANZEN, H.** *Exercises in Gas Analysis.* Translated

from the first German edition, with corrections and additions by the author, by Thomas Callan. 30 diagrams.  $5 \times 7\frac{1}{4}$ . cloth. 127 pp. net, \$1.00

**FRITSCH, J.** *The Manufacture of Chemical Manures.* Translated from the French, with numerous notes, by Donald Grant. 69 illus., 108 tables. 8vo. cloth. 355 pp. net, \$4.00

**GROSSMANN, J.** *Ammonia and Its Compounds.* Illustrated. 12mo. cloth. 151 pp. net, \$1.25

**HALE, WILLIAM J.** *Calculations in General Chemistry.* With definitions, explanations and problems. *Fifth Edition, revised.* 12mo. cloth. 185 pp. net, \$1.00

**HALL, CLARE H.** *Chemistry of Paints and Paint Vehicles.* 8vo. cloth. 141 pp. net, \$2.00

**HERING, C., and GETMAN, F. H.** *Standard Tables of Electrochemical Equivalents and Their Derivatives.* Illustrated.  $4\frac{1}{2} \times 7\frac{1}{2}$ . cloth. 140 pp. net, \$2.00

**HILDITCH, T. P.** *A Concise History of Chemistry.* 16 diagrams. 12mo. cloth. 273 pp. net, \$1.25

**HILL, C. W.** *Laboratory Manual and Notes in Beginning Chemistry.* *Second Revised Edition.* In Press

**HOYT, W. F.** *Chemistry by Experimentation, Including Qualitative Analysis.* A laboratory manual for the first year course. In Press

**HÜBNER, JULIUS.** *Bleaching and Dyeing of Vegetable Fibrous Materials.* 95 illus. (many in two colors). 8vo. cloth. 457 pp. net, \$5.00

**HUDSON, O. F.** *Iron and Steel.* An introductory textbook for engineers and metallurgists. With a section on Corrosion by Guy D. Bengough. 47 illus. 8vo. cloth. 184 pp. net, \$2.00

**HURST, GEO. H.** *Lubricating Oils, Fats and Greases.* Their origin, preparation, properties, uses, and analysis. *Third Edition, revised and enlarged,* by Henry Leask. 74 illus. 8vo. cloth. 405 p. net, \$4.00

- HURST, G. H., and SIMMONS, W. H.** Textile Soaps and Oils. *Second Edition, revised and partly rewritten.* 11 illustrations.  $5\frac{1}{2} \times 8\frac{3}{4}$ . 204 pp. net, \$3.00
- HYDE, FREDERIC S.** Solvents, Oils, Gums, Waxes and Allied Substances.  $5\frac{1}{4} \times 8\frac{1}{2}$ . cloth. 182 pp. net, \$2.00
- INGLE, HERBERT.** Manual of Agricultural Chemistry. Illustrated. 8vo. cloth. 388 pp. net, \$3.00
- JOHNSTON, J. F. W.** Elements of Agricultural Chemistry. Revised and rewritten by Charles A. Cameron and C. M. Aikman. *Nineteenth Edition.* Illustrated. 12mo. cloth. 502 pp. \$2.60
- JONES, HARRY C.** A New Era in Chemistry. Some of the more important developments in general chemistry during the last quarter of a century. Illustrated. 12mo. cloth. 336 pp. net, \$2.00
- **The Nature of Solution.** Edited by E. E. Reid. Illustrated. 6 x 9. cloth. 406 pp. net, \$3.50
- KEMBLE, W. F., and UNDERHILL, C. R.** The Periodic Law and the Hydrogen Spectrum. Illustrated. 8vo. paper. 16 pp. net, \$0.50
- KERSHAW, J. B. C.** Fuel, Water, and Gas Analysis, for Steam Users. 50 ill. 8vo. cloth. 178 pp. net, \$2.50
- **Electro-Thermal Methods of Iron and Steel Production.** With an introduction by Dr. J. A. Fleming, F.R.S. 50 tables, 92 illustrations.  $5\frac{1}{2} \times 8\frac{3}{4}$ . cloth. 262 pp. net, \$3.00
- KNOX, JOSEPH.** Physico-chemical Calculations. 12mo. cloth. 196 pp. net, \$1.00
- **The Fixation of Atmospheric Nitrogen.** Illustrated.  $5 \times 7\frac{1}{2}$ . cloth. 120 pp. (Van Nostrand's Chemical Monographs.) net, \$0.75
- KOLLER, T.** Cosmetics. A handbook of the manufacture, employment and testing of all cosmetic materials and cosmetic specialties. Translated from the German by Charles Salter. 8vo. cloth. 262 pp. net, \$2.50



— **Utilization of Waste Products.** A treatise on the rational utilization, recovery and treatment of waste products of all kinds. *Second Revised and Enlarged Edition.* 22 illustrations.  $5\frac{3}{4} \times 8\frac{3}{4}$ . cloth. 336 pp. net, \$3.00

**KOPPE, S. W.** **Glycerine.** Its introduction, uses and examination. For chemists, perfumers, soapmakers, pharmacists, and explosives technologists. 7 illustrations.  $5\frac{3}{4} \times 7\frac{1}{2}$ . 260 pp. net, \$2.50

**KREMANN, R.** **The Application of Physico-chemical Theory to Technical Processes and Manufacturing Methods.** Authorized translation by Harold E. Potts, M.Sc. 35 diagrams. 8vo. cloth. 215 pp. net, \$2.50

**KRETSCHMAR, KARL.** **Yarn and Warp Sizing in All Its Branches.** Translated from the German by C. Salter. 122 illus. 8vo. cloth. 192 pp. net, \$4.00

**LAMBORN, L. L.** **Modern Soaps, Candles and Glycerin.** 224 illustrations. 8vo. cloth. 700 pp. net, \$7.50

— **Cotton Seed Products.** 79 illus. 8vo. cloth. 253 pp. net, \$3.00

**LASSAR-COHN.** **Introduction to Modern Scientific Chemistry.** In the form of popular lectures suited for University Extension students and general readers. Translated from the *Second German Edition* by M. M. Pattison Muir. Illus. 12mo. cloth. 356 pp. net, \$2.00

**LETTIS, E. A.** **Some Fundamental Problems in Chemistry: Old and New.** 44 illustrations. 8vo. cloth. 236 pp. net, \$2.00

**LLOYD, STRAUSS L.** **Fertilizer Materials.** *In Press*

**LUNGE, GEORGE.** **Technical Methods of Chemical Analysis.** Translated from the *Second German Edition* by Charles A. Keane, with the collaboration of eminent experts. Complete in three volumes. Six parts. 448 illustrations.  $6\frac{1}{2} \times 9\frac{1}{2}$ . cloth. 3494 pp. net, \$48.00

- Vol. I. (in two parts). 201 illustrations.  $6\frac{1}{2} \times 9\frac{1}{2}$  cloth. 1024 pp. net, \$15.00
- Vol. II. (in two parts). 149 illustrations.  $6\frac{1}{2} \times 9\frac{1}{2}$  cloth. 1294 pp. net, \$18.00
- Vol. III. (in two parts). 98 illustrations.  $6\frac{1}{2} \times 9\frac{1}{2}$  cloth. 1174 pp. net, \$18.00
- **Technical Chemists' Handbook.** Tables and methods of analysis for manufacturers of inorganic chemical products. *Second Edition, revised.* Illus. 12mo. leather. 276 pp. net, \$3.50
- **Coal, Tar and Ammonia.** *Fifth and Enlarged Edition.* In three volumes, not sold separately. Ill.  $6 \times 9$  cloth. 1600 pp. net, \$18.00
- **The Manufacture of Sulphuric Acid and Alkali.** A theoretical and practical treatise.
- Vol. I. Sulphuric Acid. *Fourth Edition, enlarged.* In three parts, not sold separately. 543 illustrations. 8vo. cloth. 1665 pp. net, \$18.00
- **Sulphuric and Nitric Acid.** Supplement to Vol. I. *Fourth Edition.* Illustrated.  $6 \times 9$  cloth. 347 pp. net, \$5.00
- Vol. II. Sulphate of Soda, Hydrochloric Acid, Leblanc Soda. *Third Edition, much enlarged.* In two parts, not sold separately. 335 illustrations. 8vo. cloth. 1044 pp. net, \$15.00
- Vol. III. Ammonia Soda. Various Processes of Alkali-making, and the Chlorine Industry. 181 illustrations. 8vo. cloth. 784 pp. net, \$10.00
- Vol. IV. Electrolytical Methods. In Press.
- **Technical Gas Analysis.** 143 illustrations.  $6 \times 9$  cloth. 422 pp. net, \$4.00
- McINTOSH, JOHN G.** The Technology of Sugar. *Third Edition, revised and enlarged.* 244 illustrations.  $6 \times 8\frac{3}{4}$ . 540 pp. \$5.00
- McINTOSH, JOHN G.** The Manufacture of Varnish and

- Kindred Industries.** Illus. 8vo. cloth. In 3 volumes.  
 Vol. I. Oil Crushing, Refining and Boiling; Manufacture of Linoleum; Printing and Lithographic Inks; India Rubber Substitutes. 29 illus. 160 pp. net, \$3.50  
 Vol. II. Varnish Materials and Oil Varnish Making. 66 illus. 216 pp. net, \$4.00  
 Vol. III. Spirit Varnishes and Varnish Materials. 64 illus. 492 pp. net, \$4.50
- MARTIN, G.** *Triumphs and Wonders of Modern Chemistry.* A popular treatise on modern chemistry and its marvels written in non-technical language. 76 illustrations. 12mo. cloth. 358 pp. net, \$2.00
- *Modern Chemistry and Its Wonders.* A popular account of some of the more remarkable recent advances in chemical science. 65 illustrations.  $5\frac{1}{4} \times 7\frac{3}{4}$ . 267 pp. \$2.00
- MELICK, CHARLES W.** *Dairy Laboratory Guide.* 52 illustrations. 12mo. cloth. 135 pp. net, \$1.25
- MERCK, E.** *Chemical Reagents: Their Purity and Tests.* *Second Edition, revised.* 6 x 9. cloth. 210 pp. \$1.00
- MIERZINSKI, S.** *The Waterproofing of Fabrics.* Translated from the German by A. Morris and H. Robson. *Second Edition, revised and enlarged.* 29 illustrations.  $5 \times 7\frac{1}{2}$ . 140 pp. net, \$2.50
- MITCHELL, C. A.** *Mineral and Aerated Waters.* 111 illustrations. 8vo. cloth. 244 pp. net, \$3.00
- MITCHELL, C. A., and PRIDEAUX, R. M.** *Fibres Used in Textile and Allied Industries.* 66 illustrations. 8vo. cloth. 208 pp. net, \$3.00
- MUNBY, A. E.** *Introduction to the Chemistry and Physics of Building Materials.* Illus. 8vo. cloth. 365 pp. (Van Nostrand's Westminster Series.) net, \$2.00
- MURLAY, J. A.** *Soils and Manures.* 33 illustrations. 8vo. cloth. 367 pp. (Van Nostrand's Westminster Series.) net, \$2.00



- NEAVE, G. B., and HEILBRON, I. M.** The Identification of Organic Compounds. 12mo. cloth. 111 pp.  
net, \$1.25
- NORTH, H. B.** Laboratory Experiments in General Chemistry. *Second Edition, revised.* 36 illustrations.  
 $5\frac{1}{4} \times 7\frac{3}{4}$ . cloth. 212 pp. net, \$1.00
- OLSEN, J. C.** A Textbook of Quantitative Chemical Analysis by Gravimetric and Gasometric Methods. Including 74 laboratory exercises giving the analysis of pure salts, alloys, minerals and technical products. *Fifth Edition, revised and enlarged.* Illustrated.  
 $6\frac{1}{2} \times 9\frac{1}{4}$ . cloth. 576 pp. net, \$3.50
- PARRY, ERNEST J.** The Chemistry of Essential Oils and Artificial Perfumes. *Second Edition, thoroughly revised and greatly enlarged.* Illustrated. 8vo. cloth.  
554 pp. net, \$5.00
- Food and Drugs. In 2 volumes. Illus. 8vo. cloth.  
Vol. I. The Analysis of Food and Drugs (Chemical and Microscopical). 59 illus. 724 pp. net, \$7.50  
Vol. II. The Sale of Food and Drugs Acts, 1873-1907. 184 pp. net, \$3.00
- PARTINGTON, JAMES R.** A Text-book of Thermodynamics (with special reference to Chemistry). 91 diagrams. 8vo. cloth. 550 pp. net, \$4.00
- Higher Mathematics for Chemical Students. 44 diagrams. 12mo. cloth. 272 pp. net, \$2.00
- PERKIN, F. M., and JAGGERS, E. M.** Textbook of Elementary Chemistry. 77 illustrations.  $4\frac{3}{4} \times 7$ . cloth.  
342 pp. net, \$1.00
- PLATTNER'S** Manual of Qualitative and Quantitative Analysis with the Blowpipe. *Eighth Edition, revised.* Translated by Henry B. Cornwall, assisted by John H. Caswell, from the *Sixth German Edition*, by Friedrich Kolbeck. 87 ill. 8vo. cloth. 463 pp. net, \$4.00

- POLLEYN, F.** Dressings and Finishings for Textile Fabrics and Their Application. Translated from the *Third German Edition* by Chas. Salter. 60 illustrations. 8vo. cloth. 279 pp. net, \$3.00
- POPE, F. G.** Modern Research in Organic Chemistry. 261 diagrams. 12mo. cloth. 336 pp. net, \$2.25
- PORRITT, B. D.** The Chemistry of Rubber. 5 x 7½. cloth. 100 pp. (Van Nostrand's Chemical Monographs.) net, \$0.75
- POTTS, HAROLD E.** Chemistry of the Rubber Industry. 8vo. cloth. 163 pp. net, \$2.00
- PRESCOTT, A. B.** Organic Analysis. A manual of the descriptive and analytical chemistry of certain carbon compounds in common use. *Sixth Edition*. Illustrated. 8vo. cloth. 533 pp. \$5.00
- PRESCOTT, A. B., and JOHNSON, O. C.** Qualitative Chemical Analysis. *Seventh Edition, revised and enlarged* by John C. Olsen, A.M., Ph.D. 6¾ x 9½. cloth. 440 pp. net, \$3.50
- PRESCOTT, A. B., and SULLIVAN, E. C.** First Book in Qualitative Chemistry. For studies of water solution and mass action. *Eleventh Edition, entirely rewritten*. 12mo. cloth. 150 pp. net, \$1.50
- PRIDEAUX, E. B. R.** Problems in Physical Chemistry with Practical Applications. 13 diagrams. 8vo. cloth. 323 pp. net, \$2.00
- RICHARDS, W. A., and NORTH, H. B.** A Manual of Cement Testing. For the use of engineers and chemists in colleges and in the field. 56 illustrations. 12mo. cloth. 147 pp. net, \$1.50
- RIDEAL, S.** Glue and Glue Testing. *Second Edition, revised and enlarged*. 14 illustrations. 5¾ x 8¾. cloth. 194 pp. net, \$4.00

- ROGERS, ALLEN** (Editor). *Industrial Chemistry*. A manual for the student and manufacturer. *Second Edition, thoroughly revised and enlarged*. Written by a staff of eminent specialists. 304 illustrations.  $6\frac{1}{2} \times 9\frac{3}{4}$ . cloth. 1026 pp. net, \$5.00
- ROGERS, ALLEN**. *Elements of Industrial Chemistry*. An abridgement of *The Manual of Industrial Chemistry*. 117 illustrations, 1 folding plate.  $5\frac{1}{2} \times 8$ . 521 pp. net, \$3.00
- *A Laboratory Guide of Industrial Chemistry*. Illustrated. 8vo. cloth. 170 pp. net, \$1.50
- ROHLAND, PAUL**. *The Colloidal and Crystalloidal State of Matter*. Translated by W. J. Britland and H. E. Potts. 12mo. cloth. 54 pp. net, \$1.25
- ROTH, W. A.** *Exercises in Physical Chemistry*. Authorized translation by A. T. Cameron. 49 illustrations. 8vo. cloth. 208 pp. net, \$2.00
- SCHERER, R.** *Casein: Its Preparation and Technical Utilization*. Translated from the German by Charles Salter. *Second Edition, revised and enlarged*. Illustrated. 8vo. cloth. 196 pp. net, \$3.00
- SCHIDROWITZ, P.** *Rubber. Its Production and Industrial Uses*. Plates, 83 illus. 8vo. cloth. 320 pp. net, \$5.00
- SCHWEIZER, V.** *Distillation of Resins, Resinate Lakes and Pigments*. Illustrated. 8vo. cloth. 183 pp. net, \$3.50
- SCOTT, W. W.** *Qualitative Chemical Analysis*. A laboratory manual. *Second Edition, thoroughly revised*. Illus. 8vo. cloth. 180 pp. net, \$1.50
- SCOTT, W. W.** (Editor). *Standard Methods of Chemical Analysis*. Ill.  $6 \times 9$ . 900 pp. net, \$8.00
- SCUDDER, HEYWARD**. *Electrical Conductivity and Ionization Constants of Organic Compounds*.  $6 \times 9$ . cloth. 575 pp. net, \$3.00



- SEARLE, ALFRED B.** *Modern Brickmaking.* 260 illustrations. 8vo. cloth. 449 pp. net, \$5.00
- **Cement, Concrete and Bricks.** 113 illustrations.  $5\frac{1}{2} \times 8\frac{1}{4}$ . cloth. 415 pp. net, \$3.00
- SEIDELL, A.** *Solubilities of Inorganic and Organic Substances.* A handbook of the most reliable quantitative solubility determinations. *Second Printing, corrected.* 8vo. cloth. 367 pp. net, \$3.00
- SEETER, G.** *Outlines of Physical Chemistry. Second Edition, revised.* Illus. 12mo. cloth. 401 pp. \$1.75
- **A Text-book of Inorganic Chemistry.** 90 illustrations. 12mo. cloth. 595 pp. net, \$1.75
- SEXTON, A. H.** *Fuel and Refractory Materials. Second Ed., revised.* 104 illus. 12mo. cloth. 374 pp. net, \$2.00
- **Chemistry of the Materials of Engineering.** Illus. 12mo. cloth. 344 pp. net, \$2.50
- SIMMONS, W. H., and MITCHELL, C. A.** *Edible Fats and Oils.* Their composition, manufacture and analysis. Illustrated. 8vo. cloth. 164 pp. net, \$3.00
- SINDALL, R. W.** *The Manufacture of Paper.* 58 illus. 8vo. cloth. 285 pp. (Van Nostrand's Westminster Series.) net, \$2.00
- SINDALL, R. W., and BACON, W. H.** *The Testing of Wood Pulp.* A practical handbook for the pulp and paper trades. Illus. 8vo. cloth. 150 pp. net, \$2.50
- SMITH, J. C.** *The Manufacture of Paint.* A manual for paint manufacturers, merchants and painters. *Second Edition, revised and enlarged.* 80 illustrations  $5\frac{1}{2} \times 8\frac{3}{4}$ . cloth. 286 pp. net, \$3.50
- SMITH, W.** *The Chemistry of Hat Manufacturing.* Revised and edited by Alber. Shonk. Illustrated. 12mo. cloth. 132 pp. net, \$3.00
- SOUTHCORBE, J. E.** *Chemistry of the Oil Industries.* Illus. 8vo. cloth. 209 pp. net, \$3.00

- SPEYERS, C. L.** Text-book of Physical Chemistry. 20 illustrations. 8vo. cloth. 230 pp. net, \$2.25
- SPIEGEL, L.** Chemical Constitution and Physiological Action. Translated by C. Luedeking and A. C. Boylston. 5 x 7½. cloth. 160 pp. net, \$1.25
- STEVENS, H. P.** Paper Mill Chemist. 67 illustrations. 82 tables. 16mo. cloth. 280 pp. net, \$2.50
- SUDBOROUGH, J. J., and JAMES, J. C.** Practical Organic Chemistry. 92 illustrations. 12mo. cloth. 394 pp. net, \$2.00
- TERRY, H. L.** India Rubber and Its Manufacture. 18 illustrations. 8vo. cloth. 303 pp. (Van Nostrand's Westminster Series.) net, \$2.00
- TITHERLEY, A. W.** Laboratory Course of Organic Chemistry, Including Qualitative Organic Analysis. Illustrated. 8vo. cloth. 235 pp. net, \$2.00
- TOCH, M.** Chemistry and Technology of Paints. *Second Edition, revised and enlarged.* Ill. 6 x 9. 373 pp. net, \$4.00
- TOCH, M.** Materials for Permanent Painting. A manual for manufacturers, art dealers, artists, and collectors. With full-page plates. Illustrated. 12mo. cloth. 208 pp. net, \$2.00
- TUCKER, J. H.** A Manual of Sugar Analysis. *Sixth Edition.* 43 illustrations. 8vo. cloth. 353 pp. \$3.50
- UNDERWOOD, N., and SULLIVAN, T. V.** Chemistry and Technology of Printing Inks. 9 illustrations. 6 x 9. cloth. 145 pp. net, \$3.00
- VAN NOSTRAND'S Chemical Annual.** Edited by John C. Olsen and Alfred Melhado. A handbook of useful data for analytical manufacturing and investigating chemists and chemical students. *Third Issue, enlarged.* 5 x 7½. leather. 683 pp. net, \$2.50
- VINCENT, C.** Ammonia and Its Compounds. Their

- manufacture and uses. Translated from the French by M. J. Salter. 32 ill. 8vo. cloth. 113 pp. net, \$2.00
- VON GEORGIEVICS, G.** *Chemical Technology of Textile Fibres.* Translated from the German by Charles Salter. 47 illustrations. 8vo. cloth. 320 pp. net, \$4.50
- *Chemistry of Dyestuffs.* Translated from the *Second German Edition* by Charles Salter. 8vo. cloth. 412 pp. net, \$4.50
- VOSMAER, A.** *Ozone, Its Manufacture, Properties and Uses.* 75 illustrations. 6 x 9. cloth. 210 pp. net, \$2.50
- WADMORE, J. M.** *Elementary Chemical Theory.* Illus. 12mo. cloth. 286 pp. net, \$1.50
- WALKER, JAMES.** *Organic Chemistry for Students of Medicine.* Illus. 6 x 9. cloth. 328 pp. net, \$2.50
- WALSH, J. J.** *Mining and Mine Ventilation.* 26 illus. 8vo. cloth. 192 pp. net, \$2.00
- WARNES, A. B.** *Coal Tar Distillation and Working Up of Tar Products.* 67 illustrations. 5¾ x 8¾. cloth. 197 pp. net, \$2.50
- WHITE, C. H.** *Methods in Metallurgical Analysis.* 106 illustrations. 5 x 7½. cloth. 365 pp. net, \$2.50
- WHITE, G. F.** *A Laboratory and Class-room Guide to Qualitative Chemical Analysis.* 5 x 7. cloth. 178 pp. net, \$1.25
- WILSON, F. J., and HEILBRON, I. M.** *Chemical Theory and Calculations.* An elementary text-book. Illus., 3 folding plates. 12mo. cloth. 145 pp. net, \$1.00
- WOOD, J. K.** *The Chemistry of Dyeing.* 5 x 7½. cloth. 87 pp. (Van Nostrand's Chemical Monographs.) net, \$0.75
- WORDEN, E. C.** *The Nitrocellulose Industry.* A com-



pendium of the history, chemistry, manufacture, commercial application, and analysis of nitrates, acetates, and xanthates of cellulose as applied to the peaceful arts. With a chapter on gun cotton, smokeless powder and explosive cellulose nitrates. Illustrated. 8vo. cloth. Two volumes. 1239 pp. net, \$10.00

— **Technology of Cellulose Esters.** A theoretical and practical treatise on the origin, history, chemistry, manufacture, technical application and analysis of the products of acylation and alkylation of normal and modified cellulose, including nitrocellulose, celluloid, pyroxylin, collodion, celloidin, gun-cotton, acetylcellulose and viscose, as applied to technology, pharmacy, microscopy, medicine, photography and the warlike and peaceful arts. *In ten volumes.* 600 ill.; 12 plates, 110,000 patent and literature references to the work of 12,000 investigators.

**Vol. VIII. Carbohydrate Carboxylates (Cellulose Acetate).** Illustrated.  $6\frac{1}{2} \times 9\frac{1}{2}$ . 515 pp. net, \$5.00  
(Other volumes to follow at short intervals.)

**WREN, HENRY.** **Organometallic Compounds of Zinc and Magnesium.**  $5 \times 7\frac{1}{2}$ . cloth. 108 pp. (Van Nostrand's Chemical Monographs.) net, \$0.75

# D. VAN NOSTRAND COMPANY

---

are prepared to supply, either from  
their complete stock or at  
short notice,

## Any Technical or Scientific Book

In addition to publishing a very large  
and varied number of SCIENTIFIC AND  
ENGINEERING BOOKS. D. Van Nostrand  
Company have on hand the largest  
assortment in the United States of such  
books issued by American and foreign  
publishers.

---

All inquiries are cheerfully and care-  
fully answered and complete catalogs  
sent free on request.

---

25 PARK PLACE

NEW YORK







LOAN PERIOD	1	2	3
Home Use			
	4	5	6

Renewals and Recharges may be made 4 days prior to the due date.  
Books may be renewed by calling 642-3405.

[illegible]

UNIVERSITY OF CALIFORNIA, BERKELEY  
Berkeley, California 94720-6000

YC 18444

U. C. BERKELEY LIBRARIES



C051326950



